MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

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A STUDY OF INTUMESCENT REACTION MECHANISMS
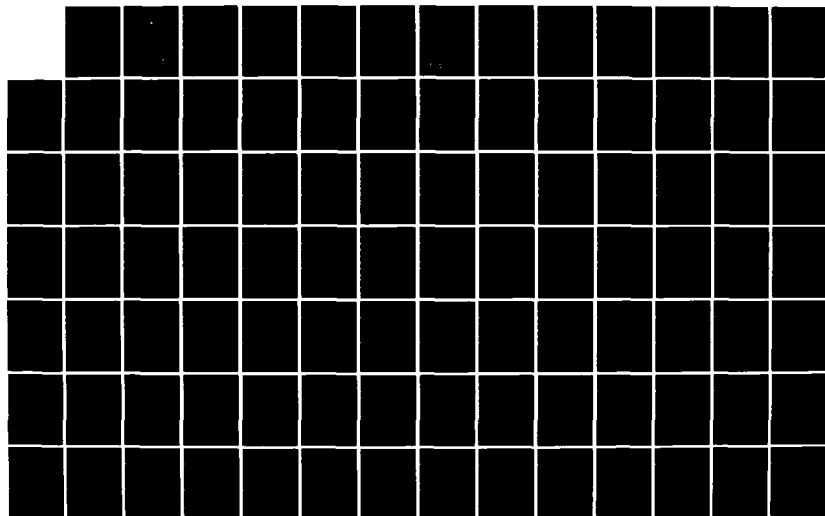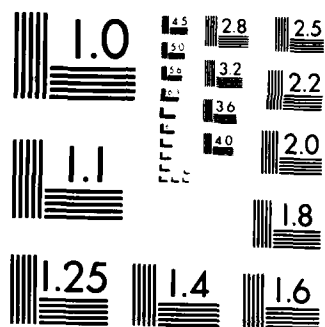
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An extensive experimental program has been conducted on intumescent systems where the components have been systematically varied. Small plates were coated with the various formulations, exposed to a heat source typical of aviation fuel fires, and the temperature-time history of the substrate recorded. Concurrently, a simplified mathematical model was developed for an intumenscing system which has given insight to the fundamental mechanisms of intumescence. The model and the results of the experimental program demonstrated certain desirable features of intumescent systems and hold the promise of guiding the optimization of certain promising formulations to thermally protect Navy ordnance.

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ACKNOWLEDGEMENTS

1.0 INTRODUCTION

In 1969, the U. S. Navy established the Weapons Cook-Off Improvement Program to protect bombs, missiles, rockets and other ordnance from fires, such as an aviation fuel fire resulting from an accident on a carrier deck. This program was established to accomplish two specific objectives: delay the ordnance reaction for at least five minutes and limit the extent of the reaction to a deflagration (case rupture and burning of explosive). Since then, the five-minute delay has been achieved successfully primarily through the use of ablative and intumescent coatings on the exterior skin of various bombs, rocket launchers, mines, missiles, etc. Intumescent systems, as used throughout this report, refer to systems which swell (i.e., intumesce) when subjected to heat such as from a fire. Typically, an intumescent system consists of an intumescent filler, a binder which "packages" the system and provides general purpose environmental considerations such as adhesion and weatherability, and a small quantity of material referred to as a bridging agent or fiber which can add integrity to the char after intumescence.

Previous work [1,2,3] focused on developing an analytic model to describe intumescing systems. A mathematical model was developed which described the various physical processes by considering mass and energy control volumes. Expansion was accounted for by assuming it to be a function of mass loss. Thermodynamic data from thermogravimetric analysis and differential scanning calorimetry characterized the chemical constituents of the coating system. A computer program was written to solve the system of equations, with appropriate boundary conditions, as a function of time. Mass loss, temperature, expansion velocity, etc., were computed and model calculations compared against experimental data. Strengths and weaknesses of the model were assessed and discussed. Though intumescent coatings are the material of choice whenever high insulation efficiency from a limited film thickness is desired [4], there is considerable interest in achieving a better understanding of intumescent reaction mechanisms in the hope of improving their ability to protect weapons in the current Navy inventory [5]. This report documents experi-

mental and analytical work performed in pursuit of better understanding
of intumescent reaction mechanisms.

The objectives of this research effort were to vary systematically
intumescent formulations and develop a procedure for optimizing a parti-
cular formulation. This experimental work furnished information on
intumescent coating systems that were previously unavailable and gener-
ated data that advanced our understanding of intumescent reaction mech-
anisms. Additionally, a simplified mathematical model involving certain
approximations was developed to permit rapid and economical exploration
of some features predicted by the more detailed model of Reference 1.
The rest of this report is divided into four main topic areas: a dis-
cussion of the experimental program; a discussion of the simplified
mathematical model, referred to as the Frontal Model; an analysis of
the experimental results, particularly in light of the insights provided
by the Frontal Model; and finally the summar   onclusions, and recom-
mendations for further work.

2.0 EXPERIMENTAL PROGRAM

2.1 Baseline Formulation

The previous work [1] focused on an intumescent formulation developed by NASA which the Navy has found to be effective in protecting ordnance from fires. Table 1 lists the constituents of this formulation, designated as NASA formulation EX-1C-82. The binder is an epoxy resin, and since epoxies tend to be very hard and brittle, polysulfide has been added to make the binder more flexible. In earlier formulations asbestos was used as the bridging agent but glass fiber has been substituted because of the well-documented health risk associated with asbestos. The intumescing agent is the hydrated salt sodium tetraborate decahydrate, commonly called borax.

Table 2 gives the basic formulation of EX-1C-82. Because the binder is an epoxy, the system is prepared in two parts; one part contains the epoxy resin and the other part the curing agent. The NASA borax formulation was used as the baseline formulation throughout the study, both in the preparation of alternate intumescent systems and in the comparison of thermal protection. These other intumescent systems, described in the next section, involved the substitution of alternate components into the baseline formulation, as well as the variation of concentration of the different constituents.

2.2 Experimental Program

An extensive experimental program was conducted in which the individual constituents of an intumescent system were systematically varied. This systematic variation of components included the following:

    a. variation of fillers — binder and bridging agent were fixed;
    b. variation of binders — filler and bridging agent were fixed;
    c. variation of bridging agent — filler and binder were fixed;
    d. variation of solvents.

The procedure adopted was to substitute different constituents, one at a time, in the basic formulation given in Table 2. In addition to substitution, formulations were varied by changing the concentration of

Table 1. Baseline Formulation

Generic System	EX-1C-82
Binder	Epon 828 epoxy resin Thikol LP-3 polysulfide DMP-30 curing agent
Filler	Sodium tetraborate deca- hydrate (borax)
Fiber	Glass
Solvent	Toluene
Thikotrope (if required)	

Table 2. Intumescent Paint Formulation
(Percentage Concentration)
NASA Formulation EX-1C-82

Concentrations (% By Weight)

Component	A	B	(A+B)*
Polysulfide	39.18		21.85
DMP-30	5.64		3.15
EPON 828		50.41	22.29
Borax	54.90	49.32	52.43
Glass	0.28	0.27	0.28
Part A			55.78
Part B			44.22

*A and B mixed at a ratio (by mass) of 1.26 to 1.

a particular constituent. The intumescent systems chosen for this study consisted of established and newly formulated systems. Table 3 lists the various constituents which were considered as possible components of intumescent systems.

2.3 Screening Studies

Preliminary screening studies were performed to determine which binders and intumescing/filler agents might be best suited for testing. The chief objective of these precursory tests was to determine which components would be most suitable and would warrant further study. An 1.40 mm thick coating was the nominal thickness of an applied coating. After various representative coatings were cast, their qualitative thermal performance was evaluated as well as observational data on pot life, cure time, workability, flexibility, and adhesion. The coatings were applied to a metal substrate; the cured specimens then were sub-jected to heat by exposure to a Bunsen burner. A thermocouple was mounted on the rear surface of the metal substrate to give a semi-quantitative measure of the thermal performance. The preliminary test results are given in Section A1 of Appendix A.

2.4 Formulations Components

Individual components were evaluated on the basis of performance, cost, and individuality. For example, a number of inert fillers and/or fire retardants were considered. However, only one of each was chosen for full parametric evaluations. The major components (binders and intumescing agents) were more closely scrutinized since they con-stitute the main reasons for success or failure of a coating formula-tion. As a result of the screening studies, four fillers, three of the binders, and three of the fibers were dropped and not considered for further study. (Asbestos is used in some current intumescent systems, but was eliminated from this study, not for technical reasons, but because of health risks.) The materials selected to comprise the components of various formulations are listed in Table 4. The open circles in Table 4 designate alternate materials which were tested in a formulation, but with no parametric variations in concentrations.

Table 3. Components Considered for Intumescent Systems

Intumescing Agents and Fillers Considered

Aluminum Hydroxide
Aluminum Sulfate Hexadecahydrate
Ammonium Nitrate
Ammonium Phosphate
Ammonium Salt of 4-nitroaniline-2-
  sulfonic Acid (NASA Salt)
Silicon Dioxide (Inert Filler -
  Syloid 244)
Slate and Limestone Fillers

Sodium Metaborate
Sodium Metasilicate Penta-
  hydrate
Sodium Tetraborate Decahy-
  drate (Borax)
Sodium Sulfate Decahydrate
  (Glauber's Salt)
Triphenyl Phosphite
Zinc Metaborate
Borax/Sodium Metasilicate

Binders Considered

Aromatic Polyurethane Resin
Flexible Epoxy
Foundrez/Epoxy
Neoprene

Polysulfide/Epoxy
PVC
Waterglass

Fibers Considered

Asbestos
Kevlar
Glass Fiber
Graphite

Metal Fiber (Steel Wool)
Mica
Mineral Wool
Refrasil

Table 4.   Formulations Components

<u>Binders</u>   <u>Fibers (Bridging Agents)</u>

● Polysulfide-Epoxy   ● Glass Flake
● Neoprene   ● Graphite
o Foundrez/Epoxy   ● Kevlar
o Flexible Epoxy   ● Metal Fiber (Steel Wool)
                                       ● Mineral Wool

<u>Fillers</u>

● Borax
● Sodium Metasilicate
● Ammonium Phosphate
● Aluminum Sulfate Hexadecahydrate
● Inert Filler (Powdered Silica)
● Glauber's Salt
● NASA Intumescent Salt
o Borax/Sodium Metasilicate
o Zinc Metaborate
o Aluminum Hydroxide

Particular characteristics of the various components are given in Section A2 of Appendix A, as well as the reasons some components were eliminated from further study.

2.5 Experimental Matrices

Test matrices incorporating the chosen materials are given in Tables 5 through 9. An attempt was made to generate a testing program that would give data suitable for intumescent system modeling, furnish information on intumescent coatings that were previously unavailable, and generate data that would advance our understanding of intumescent reaction mechanisms.

Once the components to be used were selected, baseline formulations were established which could be modified successfully to fit the test matrix. (No attempt was made to optimize a particular coating formulation in terms of pot life, curing time, workability, ease of application, etc.) The main emphasis during the baseline formulation was on the relative concentrations of the binders and filler since they most affect coating workability. To establish the baseline formulations, each of the resin systems with various fillers was cast onto aluminum sheet material till a recipe yielded a proper average workability. In all the tables, "Formula" essentially refers to the basic NASA formulation given in Table 2, though substitutions are made for specific constituents. The rows designated "+5%," +10%," etc., refer to the percent change in mass of the specific constituent being varied. For example, if 28g of borax is used in the formula (Table A15), then the +10% formulation has 30.8g of borax with all other constituents held constant. Section A4 of Appendix A gives the actual formulation applied to each plate. (Plates 513 and 514 will be used as a reference against which the transient thermal performance of the various coating systems will be compared. More will be said about this in Section 4.)

An identifier for each test plate is given in Tables 5 through 9; these "ID" numbers are used throughout the report to identify a particular formulation. The steel test plates, depicted in Figure 2-1 were constructed by cutting out a round disc from the center of each panel, shaving 1.34 mm from the circumference, and then cementing the disc back

Table 5.   Various Fillers of Different Concentration: Test ID No.
(Binder and Fiber Constant)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	511	521	531	541	551	561	571			
+ 5%	512	522	532	542	552	562	572			
Formula	513[a]	523	533	543	553	563	573	583	593	503
- 5%	514	524	534	544	554	564	574			
-10%	515	525	535	545	555	565	575			
					Binder: Neoprene Fiber : Glass Fiber					
Formula	516[b]	526	536	546	556	566	576	586	596	506

a,b Cast two extra plates for each, one thicker and one thinner than nominal coating thickness.
     ID suffix is 'H' for more (thicker) coating; 'L' for less (thinner) coating [e.g., 513H, 513M, etc.]

Table 6.   Variation of Fibers: Test ID No.
            (Binder and Filler Constant)

            Binder: Polysulfide/Epoxy
            Filler: Borax
                     Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	513	621	631	641	651
SMS	523	622	632	642	652

Table 7.   Variation of Binders of Different Concentration: Test ID No.
            (Fiber and Filler Constant)

            Filler: Borax
            Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	711	721			
+ 5%	712	722			
Formula	513	516	a	743	753
− 5%	714	724			
−10%	715	725			

            Filler: Sodium Metasilicate (SMS)
            Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	523	526	736	746	756

---

a Borax is incompatible with Foundrez.

Table 8.   Variation of Solvent: Test ID No.
(Binder, Filler, and Fiber Constant)

Binder: Polysulfide/Epoxy
         Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	811	821	851
Neoprene	832	842	852

Table 9.   Variation of Fiber to Filler Concentration: Test ID No.
(Binder Constant)

Binder: Polysulfide/Epoxy
Filler: Borax
         SMS
Fiber : Glass Fiber and Graphite

Borax	Glass Fiber					Graphite				
	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			931							
+10			511							
0	913	923	513	943	953	963	973	621	993	903
-10			515							
-20			935							
SMS										
+20			936							
+10			521							
0			523							
-10			525							
-20			930							

Figure 2-1. Schematic of Test Plate and Holder Configuration
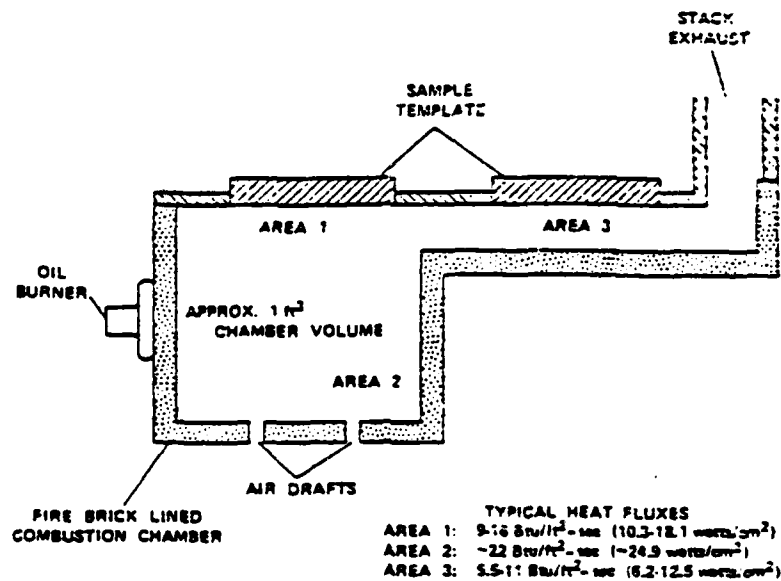
Figure 2-2. Schematic of Thermal Test Facility

in place with a high temperature epoxy adhesive. This serves to insulate
the disc from heat being conducted away to the mounted edges of the
plate; that is, this procedure essentially makes the heat transfer one
dimensional through the center section of the test plate. The coating
to be tested was applied to the plate; a mold was devised (Section A3,
Appendix A) in an attempt to get a uniform coating thickness of 1.78 mm
on all the test plates. However, even with the mold, the large varia-
tion in coating viscosities and shrinkage during curing resulted in an
average thickness of 1.845 mm but with a standard deviation from the
mean of 0.346 mm. In hindsight, more attention should have been given
to coating thickness, such as machining (e.g., wet-sanding) to achieve
a uniform thickness among all sample plates. A total of 104 plates
were coated at SwRI and sent to the Naval Air Development Center (NADC)
for testing. At NADC, two chromel-alumel thermocouples were attached
to the center section of the test plate prior to testing; the emf out-
put as a function of time was plotted directly as temperature versus
time on a chromel-alumel compensated chart recorder. The plates were
placed in a furnace-type device similar to the NASA T-3 firebox which
consists of an 0.028 cubic meter furnace (approximately cubic in con-
figuration) lined with fire brick and enclosing a horizontal rotary oil
burner of the mechanical atomization type capable of usign JP-4 or JP-5
aviation fuel, Figure 2-2. During operation, air is circulated from two
vents on the lower side up through the furnace by an overhead exhaust
fan. The heat flux, somewhat typical of what might be encountered in
an aviation fuel fire, is 2.7 cal/cm^2-s (10 BTU/ft^2-s) at the test
panels, with approximately 90 percent of the incident flux being radia-
tive [4].

2.6 Initial Conditions and Test Results

The test results were returned to SwRI for analysis. A data sheet
was prepared for each plate with space provided for such information
as initial and final plate masses, initial and final coating thicknesses,
and relevant comments concerning each test. The information contained
in these data sheets are summarized in tabular form:

a. Initial coating weight (grams) . . . . Tables 10-14;

b. Ratio of Remaining to Initial Weight . . . . Tables 15-19;

c. Initial Coating Thickness (mm) . . . . Tables 20-24;

d. Ratio of Final to Initial Thickness . . . . Tables 25-29;

e. Time to Reach 800°F (minutes) . . . . Tables 31-35;

f. Thermal Performance to 800°F (sec/mm). . . . . . . Tables 36-40;

g. End of Intumescence [Time (Temp)]. . . . . Tables 41-45;

h. $\frac{\Delta T}{\Delta t}$ Post Intumescence (°F/min). . . . . Tables 46-50.

Tables 31-35 are self-explanatory. Thermal performance, as used here, is computed by taking the time to 800°F in seconds and dividing by the initial coating thickness*. This gives a relative number for thermal protection per unit thickness of coating. While this number can be useful for comparing the thermal performance of various insulation systems, it is not a material property; the value, for the same formulation, varies as a function of thickness. Tables 41-45 summarize a distinct feature of intumescent systems. The graphical display of temperature versus time of a substrate protected by an intumescing material displays a rather noticeable change in slope. This change in slope is associated with the arrival of the intumescing front at the substrate. Section 3 discusses the underlying physical principles of this experimental observation. Tables 41-45 give the time at which the change in slope occurs and the corresponding temperature. After this "break" or change in slope in the temperature-time curve, to a first approximation, the substrate heats linearly with time (also discussed in Section 3); the slopes of the linear portion of the curves are tabulated in Tables 46-50.

According to the comments of post-test examination of the plates (Table 30), a number of the coatings were reported to have separated from the substrate--in particular, this occurred with the sodium meta-silicate and the Glauber's salt formulations. However, examination of

---

*It is understood that the Navy uses the time to 500°F and the time to 1000°F divided by the initial coating thickness for a measure of thermal performance. We arbitrarily chose the time to 800°F for the purposes of this report.

Table 10. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

INITIAL COATING WEIGHT (grams)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	11.8	13.6	15.2	15.1	11.3	10.8	13.5			
+5%	15.0	15.4	14.0	14.5	13.7	10.9	8.3			
Formula	12.1[a]	14.4	15.2	14.1	15.5	11.1	9.0	12.6	17.0	10.8
-5%	13.9	16.1	15.7	13.0	14.5	9.4	7.0			
-10%	13.2	14.2	15.1	11.1	12.3	9.9	8.2			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	13.2[b]	14.5	15.2	10.8	5.6	6.7	8.1	13.9	11.4	5.7

[a] Thicker coating 18.6
Thinner coating 9.2

[b] Thicker coating 14.2
Thinner coating 7.6

Table 11. Variation of Fibers
(Binder and Filler Constant)

INITIAL COATING WEIGHT (grams)

Binder: Polysulfide/Epoxy
Filler: Borax
         Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	12.1	11.3	12.3	12.9	11.1
SMS	14.4	13.5	12.9	14.0	13.5

Table 12. Variation of Binders of Different Concentration
(Fiber and Filler Constant)

INITIAL COATING WEIGHT (grams)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/Epoxy	Neoprene	Foundrez Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	12.4	10.4			
+ 5%	12.2	9.1			
Formula	12.1	13.2	a	13.8	12.4
- 5%	12.5	8.8			
-10%	11.6	9.3			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/Epoxy	Neoprene	Foundrez Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	14.4	14.5	15.6	15.9	9.4

a Borax is incompatible with Foundrez.

Table 13. Variation of Solvent
(Binder, Filler, and Fiber Constant)

INITIAL COATING WEIGHT (grams)

	Binder:	Polysulfide/Epoxy
		Neoprene
	Filler:	Borax
	Fiber :	Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	13.9	13.6	12.3
Neoprene	10.0	10.5	9.7

Table 14. Variation of Fiber to Filler Concentration:
(Binder Constant)

INITIAL COATING WEIGHT (grams)

	Binder:	Polysulfide/Epoxy
	Filler:	Borax
		SMS
	Fiber :	Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			11.5							
+10			11.8							
0	11.4	12.0	12.1	12.4	12.1	11.1	9.1	11.3	9.7	10.0
-10			13.2							
-20			11.0							
SMS										
+20			12.2							
+10			13.6							
0			14.4							
-10			14.2							
-20			13.3							

Table 15. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

RATIO OF REMAINING TO INITIAL WEIGHT

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	0.475	*	0.493	*	0.442	*	0.385			
+ 5%	0.787	*	0.500	*	0.394	*	*			
Formula	0.471[a]	*	0.513	*	0.400	*	*	*	0.724	0.398
- 5%	0.460	*	0.497	0.008	0.379	*	*			
-10%	0.462	*	0.490	*	0.407	*	0.476			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	*[b]	*	*	0.352	0.750	0.955	0.469	0.597	0.904	*

* See Remarks in Table 30.
[a] Thicker coating 0.478   [b] Thicker coating *
    Thinner coating *   Thinner coating *

-19-

Table 16. Variation of Fibers:
(Binder and Filler Constant)

RATIO OF REMAINING TO INITIAL WEIGHT

Binder: Polysulfide/Epoxy
Filler: Borax
         Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	.471	.469	.423	.690	.640
SMS	*	*	*	*	*

Table 17. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

RATIO OF REMAINING TO INITIAL WEIGHT

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	.597	*			
+ 5%	*	*			
Formula	.471	*	a	*	*
- 5%	.536	*			
-10%	.560	*			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

Formula	*	*	.371	.478	*

* See Remarks in Table 30.
a Borax is incompatible with Foundrez.

Table 18. Variation of Solvent
(Binder, Filler, and Fiber Constant)

RATIO OF REMAINING TO INITIAL WEIGHT

Binder: Polysulfide/Epoxy
Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	.604	.566	.626
Neoprene	.530	*	*

Table 19. Variation of Fiber to Filler Concentration:
(Binder Constant)

RATIO OF REMAINING TO INITIAL WEIGHT

Binder: Polysulfide/Epoxy
Filler: Borax
SMS
Fiber : Glass Fiber and Graphite

| Borax | Glass Fiber | | | | | Graphite | | | | |
	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			.461							
+10			.475							
0	.474	.458	.471	*	*	*	*	.469	*	*
-10			.462							
-20			*							

SMS										
+20			*							
+10			*							
0			*							
-10			*							
-20			*							

* See Remarks in Table 30.

Table 20.   Various Fillers of Different Concentration:
(Binder and Fiber Constant)

INITIAL COATING THICKNESS (mm)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H₂O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	2.02	1.64	2.31	2.36	1.45	1.60	1.89			
+ 5%	2.41	1.98	1.88	1.98	1.91	2.03	0.89			
Formula	1.75[a]	1.91	1.92	2.20	2.36	2.06	1.04	1.66	1.65	1.72
- 5%	2.13	2.36	2.01	1.88	2.11	1.57	0.88			
-10%	2.13	1.98	2.34	2.11	1.51	1.83	1.10			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H₂O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	2.29[b]	2.53	2.57	1.93	1.19	1.21	1.22	2.21	1.32	1.45

[a] Thicker coating 2.69   Thinner coating 1.04
[b] Thicker coating 2.69   Thinner coating 1.32

Table 21. Variation of Fibers
(Binder and Filler Constant)

INITIAL COATING THICKNESS (mm)

Binder: Polysulfide/Epoxy
Filler: Borax
       Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	1.75	1.88	2.12	2.11	1.80
SMS	1.91	2.12	1.66	1.99	1.93

Table 22. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

INITIAL COATING THICKNESS (mm)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	2.12	1.78			
+ 5%	1.68	1.56			
Formula	1.75	2.29	a	1.84	2.11
- 5%	1.91	1.52			
-10%	2.02	1.61			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	1.91	2.53	2.04	1.68	1.96

a Borax is incompatible with Foundrez.

Table 23. Variation of Solvent
(Binder, Filler, and Fiber Constant)

INITIAL COATING THICKNESS (mm)

Binder: Polysulfide/Epoxy
        Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	1.75	1.91	1.80
Neoprene	1.69	1.93	1.64

Table 24. Variation of Fiber to Filler Concentration:
(Binder Constant)

INITIAL COATING THICKNESS (mm)

Binder: Polysulfide/Epoxy
Filler: Borax
        SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			1.89							
+10			2.02							
0	1.80	1.98	1.75	1.93	2.13	1.55	1.46	1.88	1.71	1.97
-10			2.13							
-20			1.45							
SMS										
+20			1.88							
+10			1.64							
0			1.91							
-10			1.98							
-20			2.11							

Table 25. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

RATIO OF FINAL TO INITIAL COATING THICKNESS

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Sylold)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	6.29	*	3.16	*	5.66	*	11.86			
+ 5%	5.60	*	3.89	*	5.08	*	19.81			
Formula	6.36[a]	*	3.83	*	2.11	*	15.46	5.87	0.76	5.66
- 5%	6.05	*	5.61	3.47	4.62	*	23.74			
-10%	6.05	*	2.80	3.09	3.27	*	14.64			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Sylold)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	*[b]	1.97	5.03	5.04	1.47	1.48	2.75	2.25	2.56	*

* See remarks in Table 30.
a Thicker coating 7.17   b Thicker coating *
   Thinner coating *   Thinner coating 2.56
b Thicker coating *
   Thinner coating 2.56

Table 26. Variation of Fibers
(Binder and Filler Constant)

RATIO OF FINAL TO INITIAL COATING THICKNESS

Binder: Polysulfide/Epoxy
Filler: Borax
         Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	6.36	7.69	3.85	4.60	*
SMS	*	*	*	*	*

Table 27. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

RATIO OF FINAL TO INITIAL COATING THICKNESS

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	7.57	*			
+ 5%	*	*			
Formula	6.36	*	a	*	*
- 5%	10.1	*			
-10%	8.75	*			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	*	1.97	3.99	2.93	*

* See Remarks in Table 30.
a Borax is incompatible with Foundrez.

Table 28. Variation of Solvent
(Binder, Filler, and Fiber Constant)

RATIO OF FINAL TO INITIAL COATING THICKNESS

Binder: Polysulfide/Epoxy
        Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	6.46	6.75	7.16
Neoprene	9.50	*	*

Table 29. Variation of Fiber to Filler Concentration:
(Binder Constant)

RATIO OF FINAL TO INITIAL COATING THICKNESS

Binder: Polysulfide/Epoxy
Filler: Borax
        SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			7.65							
+10			6.29							
0	6.28	3.30	6.36	*	*	*	*	7.69	*	*
-10			6.05							
-20			*							
SMS										
+20			*							
+10			*							
0			*							
-10			*							
-20			*							

* See Remarks in Table 30.

Table 30. Test Comments/Observations*

Test ID No.	Remarks
511	Char is uniformly smooth, convex, and hard.
512	Char is uniformly smooth, convex, and hard.
513	Char is uniformly smooth, convex, and hard.
513M	Char is uniformly smooth, convex, and hard
513L	Sample stuck to test apparatus.
514	Char is uniformly smooth, convex, and hard.
515	Char is uniformly smooth, convex, and hard.
521	Plate separated from coating.
522	Plate separated from coating.
523	Plate separated from coating.
524	Plate separated from coating.
525	Plate separated from coating.
531	Hard char has reddish, bubbly or beaded appearance.
532	Hard char has reddish, bubbly or beaded appearance.
533	Hard char has reddish, bubbly or beaded appearance.
534	Hard char has reddish, bubbly or beaded appearance.
535	Hard char has reddish, bubbly or beaded appearance.
541	Entire 2 inch center test area fell out.
542	Entire 2 inch center test area fell out.
543	Plate separated from coating.
544	Char is smooth and hard.
545	Part of smooth, hard char stuck to test apparatus.
551	Cracking and flaking in center section with entire coating charred black with between 1/2 to 1 inch long fissures parallel over entire surface.
552	Same as 551.
553	Same as 552.
554	Same as 553.
555	Same as 554.
561	Plate separated from coating.
562	Plate separated from coating.
563	Plate separated from coating.

*Comments by NADC personnel.

Table 30. (Continued)

564	Plate separated from coating.
565	Plate separated from coating.
571	Char is crusty and flakey.
572	Char is crusty and flakey. Part of coating outside of test area stuck to test apparatus.
573	Same as 572.
574	Same as 573.
575	Char is crusty and flakey.
583	Hard char has a reddish, bubbly or beaded appearance. Part of coating outside of test area stuck to test apparatus.
593	Char is hard and smooth.
503	Char is hard, but flakey.
516	Center section fell out during test while the surrounding area is sticky and fibrous.
516M	Same as 516.
516L	Coating outside of test area stuck to test apparatus.
526	Coating outside test area stuck to test apparatus while char is white with glassy beads or bubbles in test area.
536	Coating outside of test area stuck to test apparatus while char has a spongy appearance with milky, glassy substance on top.
546	Char is pure white and powdery with large cracks in test area.
556	Coating turned black.
566	Coating turned black.
576	Char is crusty with large separated cracks running through test area.
586	Char is black, hard, glassy and bubbly.
596	Char is black with cracking and some flaking.
506	Center section fell out during test.

Table 30. (Continued)

Test ID No.	Remarks
621	Char is black, hard and exhibits orange peel effect.
622	Entire char fell off test plate.
631	Char is black, hard and exhibits orange peel effect.
632	Entire char fell off test plate.
641	Char is black, hard and exhibits orange peel effect.
642	Entire char fell off test plate.
651	Char is black, hard and exhibits orange peel effect. Char crumpled upon attempt to measure thickness.
652	Entire char fell off test plate.
711	Char is black and hard and exhibits orange peel effect.
712	Char is black and hard and exhibits orange peel effect. Part of char fell off test plate.
714	Char is black and hard and exhibits orange peel effect.
715	Char is black and hard and exhibits orange peel effect.
721	Char fell off leaving a white stringy fibrous material on test plate.
722	Same as 721.
724	Same as 722.
725	Same as 724.
736	Char is hard, chalky in appearance with 5 or 6 small orange beads.
743	Char fell off test plate.
746	Char is hard, chalky in appearance with several white and orange beads.
753	Char fell off test plate. Remainder of coating was stringy and fibrous and yellowish brown in color.
756	Entire char fell off test plate.
811	Char is black and hard and exhibits orange peel effect.
821	Same as 811.
832	Gray, hard char with white fibers standing up about 9/16 of an inch on the test plate outside the char area.
842	Char fell off test plate. White fibers standing up outside char area.
851	Char is black and hard and exhibits orange peel effect.
852	Char fell off test plate. A ring of white fibers standing up about 1/2" surround the edge of the char area.

Table 30. (Continued)

Test ID No.	Remarks
913	Char is black, hard and exhibits orange peel effect.
923	Same as 913.
931	Same as 923.
935	Char is black and hard, but coating lifted off of test plate.
936	Entire char fell off test plate. Exhaust fan malfunctioned.
930	Same as 936.
943	Char is black, hard and exhibits orange peel effect. Part of char fell off test plate.
953	Entire char fell off test plate.
963	Char is black, hard and exhibits orange peel effect. Most of char fell off test plate.
973	Same as 963.
993	Same as 973.
903	Same as 993.

Table 31. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

TIME TO REACH 800°F (minutes)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	3.90	3.30	3.30	3.65	2.40	2.05	5.65			
+ 5%	4.85	3.75	3.40	3.15	2.80	2.25	3.05			
Formula	3.00[a]	4.05	3.70	3.85	2.20	2.50	4.25	2.90	2.35	2.15
- 5%	4.05	3.65	3.30	3.00	2.60	1.90	3.20			
-10%	4.40	3.70	3.70	3.25	2.05	2.05	2.95			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	1.80[b]	4.85	2.95	4.55	1.55	1.20	1.55	3.10	1.45	1.45

* See remarks in Table 30.　b Thicker coating 2.5
a Thicker coating 6.1　　　　　Thinner coating *
　Thinner coating 1.95

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Table 32. Variation of Fibers
(Binder and Filler Constant)

TIME TO REACH 800°F (minutes)

Binder: Polysulfide/Epoxy
Filler: Borax
         Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	3.00	5.50	4.65	3.70	2.75
SMS	4.05	5.90	5.40	5.41	4.80

Table 33. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

TIME TO REACH 800°F (minutes)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	3.75	1.80+(1.60)			
+ 5%	3.00	1.55+(1.50)			
Formula	3.00	1.80	a	4.50+(3.70)	3.90+(3.10)
- 5%	2.10	1.56+(1.40)			
-10%	2.42	1.52+(1.30)			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	4.05	4.85	5.18	3.98	2.70

a Borax is incompatible with Foundrez.
+ Char fell off test plate; time to 800°F estimated from slope
   of curve before coating fell off; coating fell off at (x.xx) minutes.

Table 34. Variation of Solvent
(Binder, Filler, and Fiber Constant)

TIME TO REACH 800°F (minutes)

Binder: Polysulfide/Epoxy
         Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	5.52	4.80	4.10
Neoprene	2.25	2.05+(1.80)	1.75+(1.50)

Table 35. Variation of Fiber to Filler Concentration
(Binder Constant)

TIME TO REACH 800°F (minutes)

Binder: Polysulfide/Epoxy
Filler: Borax
         SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			3.70							
+10			3.90							
0	3.25	3.60	3.00	4.20	4.10	2.85	2.76	5.50	3.65	2.90
-10			4.40							
-20			3.12							
SMS										
+20			4.80							
+10			⁓.⁓⁓							
0			4.05							
-10			3.70							
-20			5.60							

+ Char fell off test plate; time to 800°F estimated from slope
  of curve before coating fell off; coating fell off at (x.xx) minutes.

Table 36. Various Fillers of Different Concentration: (Binder and Fiber Constant)

TIME TO REACH 800°F/INITIAL COATING THICKNESS (sec/mm)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	116	121	86	93	99	77	179			
+ 5%	121	114	109	95	88	67	206			
Formula	103[a]	127	116	105	56	73	245	105	85	75
- 5%	114	93	99	80	74	73	218			
-10%	124	112	95	92	81	67	161			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	47[b]	115	69	141	78	60	76	84	66	60

[a] Thicker coating 136
Thinner coating 113

[b] Thicker coating 56
Thinner coating #

Table 37. Variation of Fibers
(Binder and Filler Constant)

TIME TO REACH 800°F/INITIAL COATING THICKNESS (sec/mm)

Binder: Polysulfide/Epoxy
Filler: Borax
        Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	103	176	132	105	92
SMS	127	195	206	163	149

Table 38. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

TIME TO REACH 800°F/INITIAL COATING THICKNESS (sec/mm)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	106	61			
+ 5%	107	60	a	147	111
Formula	103	47			
- 5%	66	62			
-10%	72	57			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	127	115	152	142	83

a Borax is incompatible with Foundrez.

Table 39. Variation of Solvent
(Binder, Filler, and Fiber Constant)

TIME TO REACH 800°F/INITIAL COATING THICKNESS (sec/mm)

Binder: Polysulfide/Epoxy
Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	189	151	137
Neoprene	80	64	64

Table 40. Variation of Fiber to Filler Concentration:
(Binder Constant)

TIME TO REACH 800°F/INITIAL COATING THICKNESS (sec/mm)

Binder: Polysulfide/Epoxy
Filler: Borax
SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			117							
+10			116							
0	108	109	103	131	115	110	113	176	128	88
-10			124							
-20			129							
SMS										
+20			153							
+10			121							
0			127							
-10			112							
-20			159							

Table 41. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

END OF INTUMESCENCE [Time(Temp)]
[Min(°F)]

Binder: Polysulfide/Epoxy
Fiber: Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	1.30(290)	1.30(260)	1.3(220)	1.30(230)	.65(260)	.60(210)	3.1(400)			
+5%	1.60(290)	1.65(260)	1.0(220)	1.05(230)	.90(260)	.65(220)	2.1(660)			
Formula	.85(290)[a]	1.85(270)	1.1(220)	1.25(230)	*	.75(220)	2.6(550)	1.25(240)	*	.85(400)
-5%	1.15(290)	1.55(270)	1.2(220)	.92(230)	.90(250)	.65(220)	2.0(570)			
-10%	1.45(290)	1.45(260)	1.3(220)	1.20(240)	*	.70(220)	2.4(630)			

Binder: Neoprene
Fiber: Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	.25(210)[b]	1.15(550)	3.15(310)	1.50(220)	*	*	*	1.70(250)	*	*

* Constant slope temperature rise
a Thicker coating 2.60(315)   Thicker coating * .70(250)
  Thinner coating .65(300)   Thinner coating ** (290)
b Chart Recorder Started late
**Chart Recorder Started late

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Table 42. Variation of Fibers
(Binder and Filler Constant)

END OF INTUMESCENCE [Time(Temp)]
[Min(^oF)]

Binder: Polysulfide/Epoxy
Filler: Borax
        Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	.85(290)	1.80(300)	1.60(300)	1.36(290)	1.0(300)
SMS	1.85(270)	1.80(250)	1.40(250)	1.50(255)	1.2(240)

Table 43. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

END OF INTUMESCENCE [Time (Temp)]
[Min(^oF)]

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	1.2(205)	.85(300)			
+ 5%	1.0(275)	.65(300)			
Formula	.85(290)	.25(210)	a	.90(230)	1.8(320)
- 5%	.82(210)	.68(290)			
-10%	.80(230)	.58(290)			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	1.85(270)	1.15(550)	1.6(235)	1.2(250)	.85(300)

a Borax is incompatible with Foundrez.

Table 44.   Variation of Solvent
(Binder, Filler, and Fiber Constant)

<u>END OF INTUMESCENCE</u> [Time(Temp)]
[Min($^{\circ}$F)]

Binder: Polysulfide/Epoxy
         Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	1.40 (250)	1.60 (310)	1.01 (270)
Neoprene	.80 (310)	.70 (290)	.60 (290)

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Table 45. Variation of Fiber to Filler Concentration:
(Binder Constant)

END OF INTUMESCENCE $\frac{[Time(Temp)]}{[Min(°F)]}$

Binder: Polysulfide/Epoxy
Filler: Borax
        SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			1.40(250)							
+10			1.30(290)							
0	1.00(240)	1.30(300)	.85(290)	1.50(320)	1.40(235)	.80(280)	.80(280)	1.80(300)	.80(220)	1.0(240)
-10			1.45(290)							
-20			1.00(290)							
SMS										
+20			1.90(300)							
+10			1.30(260)							
0			1.85(270)							
-10			1.45(260)							
-20			2.00(265)							

Table 46. Various Fillers of Different Concentration:
(Binder and Fiber Constant)

$$\frac{\Delta I}{\Delta t}$$ POST INTUMESCENCE (^{o}F/min)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	183	261	290	248	361	451	160			
+ 5%	148	251	239	236	300	416	163			
Formula	239[a]	248	230	236	401	433	143	308	300	282
- 5%	166	275	236	308	348	514	173			
-10%	166	261	245	261	348	585	275			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	349[b]	323	433	261	451	631	492	492	417	540

[a] Thicker coating 125   [b] Thicker coating 349
Thinner coating 392   Thinner coating 712

Table 47. Variation of Fibers
(Binder and Filler Constant)

<u>POST INTUMESCENCE ($^{\circ}$F/min)</u>

Binder: Polysulfide/Epoxy
Filler: Borax
         Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	239	133	181	250	286
SMS	248	143	143	143	154

Table 48. Variation of Binders of Different Concentration:
(Fiber and Filler Constant)

<u>POST INTUMESCENCE ($^{\circ}$F/min)</u>

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	200	500			
+ 5%	250	500			
Formula	239	349	a	250	250
- 5%	500	500			
-10%	333	500			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	248	323	167	167	286

a Borax is incompatible with Foundrez.

Table 49. Variation of Solvent
(Binder, Filler, and Fiber Constant)

POST INTUMESCENCE ($^{\circ}$F/min)

Binder: Polysulfide/Epoxy
         Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	125	143	167
Neoprene	454	500	500

Table 50. Variation of Fiber to Filler Concentration:
(Binder Constant)

POST INTUMESCENCE ($^{\circ}$F/min)

Binder: Polysulfide/Epoxy
Filler: Borax
        SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			222							
+10			183							
0	313	250	239	167	192	263	250	133	200	286
-10			166							
-20			200							
SMS										
+20			154							
+10			261							
0			248							
-10			261							
-20			150							

the experimental data does not warrant the conclusions that the coating always fell off during testing; perhaps in some of the instances the coating separated upon removal of the plate from the test apparatus. When the coating does separate and fall off during a test, the temperature-time curve has a very steep slope compared to the thermally protected plates—this observation will be quite apparent on some of the graphical displays to be discussed later. Some anomalies appear in the data which require further examination. Specifically, it is curious that the inert filler, Syloid, also displayed a change in slope (at approximately 260°F) for three of the specimen plates (551, 552, 554) but not the other three specimen plates (553, 555, and 556). Zinc metaborate, which is a fire retardant and is not an intumescent had a linear temperature-time plot similar to plates 553, 555 and 556. It is conjectured that absorbed water was entrained in the Syloid matrix.

What would appear to be rather drastic changes in the thermal response of the substrate (Tables 31-35) for small changes in formulation concentrations are most certainly the result of variations in initial coating thickness and thus initial mass. As discussed earlier, it was found to be very difficult to keep the initial coating thickness a constant. Further discussions on the test results will be presented in Section 4; however, considerable insight can be gained by considering first the Frontal Model.

3.0 FRONTAL MODEL

3.1 Introduction

A simplified mathematical model has been developed describing an intumescent system. This model does not replace the physical model developed and discussed in Reference 1; instead, it complements and supplements the work done in the more detailed analytic model. The model is constructed for intumescent systems in which it is assumed that the transition to the intumescent state occurs at an infinitesimally thin zone or front. While physically it is expected that the intumescing region has a finite thickness, it is not unreasonable to postulate for modeling purposes that this region is very thin compared to the rest of the coating. Characteristic of an intumescing system is that when subjected to heat such as from a fire, it begins to swell or expand, i.e., intumesce. The thermophysical history of the system must follow a specific sequence for intumescence to occur. The coating material must soften during heating so that when the temperature is reached which chemically frees the blowing agent, the coating is sufficiently pliable to expand or be "pushed" by the liberated gases. The residual or remaining mass then begins to gel and solidify into a carbonaceous char. It should be noted that the coating system may continue to lose mass as it is heated (as experimentally shown in thermogravimetric analysis), but this process only affects the final state of the residual char. Generally, the release of the blowing gases is an endothermic process requiring heat to liberate the blowing agent.

Besides the foregoing discussion, there exist a number of plausible reasons why the frontal model might be expected to be an acceptable approximation to the physics of an intumescing system. In the analytic model developed by Anderson and Wauters [1], intumescence was assumed to occur continuously as a function of mass loss. However, in their analysis, they found best agreement between model predictions and experimental results when most of the expansion occurs early in the mass

3.2 The Mathematical Model

A brief description of the essence of the frontal model, including some results of the model, will be discussed here. The mathematical details are contained in Appendix B. The model is one dimensional; the coating can be divided into two regions separated by the front, as depicted in Figure 3-1. To the left of the front, the temperature is not sufficiently high to start intumescence and the material velocity is zero. To the right of the front, intumescence has occurred, and the material is moving with a uniform and nonzero velocity, u_f. The heat equation, Equation (3-1), applies to both regions, though the convective term is not present in the region to the left of the front since u=0:

$$\rho C_p \left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} k \frac{\partial T}{\partial x} \qquad (3-1)$$

where ρ, C_p, and k are the density, specific heat and thermal conductivity, respectively. The material properties can be summarized for the two regions:

Virgin State (left region)	Char State (right region)
$m = m_o$	$m = m_f$
$\rho = \rho_o$	$\rho = \rho_f$
$u = 0$	$u = u_f$
$k = k_o$	$k = k_f$

$$(3-2)$$

Letting d represent the initial thickness of the coating, and D represent the final, or expanded thickness of the coating, then it can be shown (Appendix B) that:

$$\frac{D}{d} = \frac{\rho_o m_f}{\rho_f m_o} \qquad (3-3)$$

Now the heat equation, Equation (3-1) is solved on both sides of the front with certain jump conditions across the front. These jump conditions specify the information to connect the two regions. These connection conditions, i.e., jump conditions are:
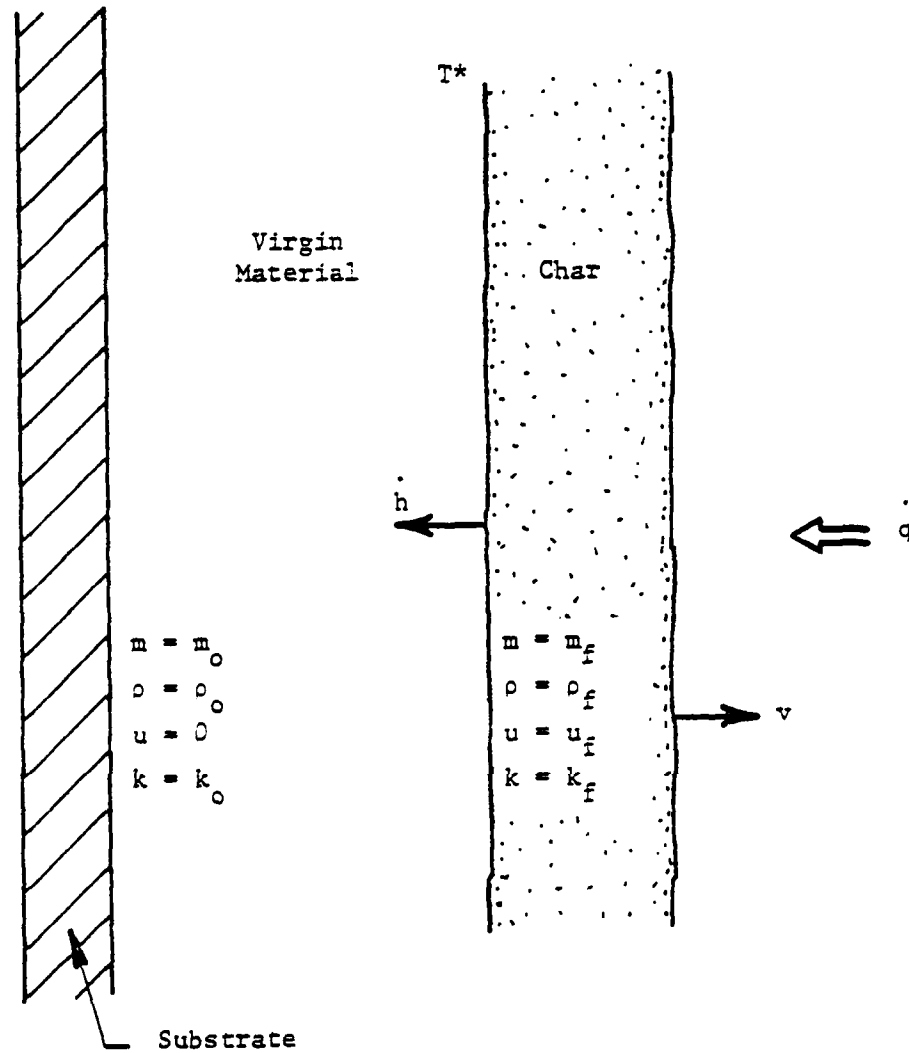
$$T^+ - T^- \equiv [T] = 0 \qquad (3-4)$$

Figure 3-1. Schematic of Frontal Model

$$T_{front} = T^*$$ (3-5)

$$[u] = u_f$$ (3-6)

The velocity jumps from 0 to u_f across the front, and likewise the thermal conductivity jumps from k_o to k_f. There is a jump condition for the heat flux also. This condition can be shown (Appendix B) to be:

$$k\frac{\partial T}{\partial x}\bigg|^{+} - k\frac{\partial T}{\partial x}\bigg|^{-} = \rho_o \dot{h} (Q - C_p T^*) (\frac{m_f}{m_o} - 1)$$ (3-7)

where Q represents the energy absorbed in an endothermic reaction, and $\dot{h}$ is defined below. The last term in Equation (3-7) represents the mass jump across the front, i.e., the mass lost by outgassing. The physical interpretation of Equation (3-7) is that heat is absorbed at the front as a consequence of outgassing and resultant mass loss. This results in a jump condition for the heat flux.

Letting h represent the location of the front, application of the conservation of mass relates the time derivative of the front location, $\dot{h}$, to the char velocity:

$$u_f = \dot{h} \left[1 - \frac{\rho_o m_f}{\rho_f m_o}\right] = \dot{h} [1 - D/d]$$ (3-8)

If L is the position of the free (outside) surface, then the following relations hold:

$$h(t=0) = d \qquad L(t=0) = d$$ (3-9)

$$h(t=t_2) = 0 \qquad L(t=t_2) = D$$ (3-10)

$$u_f = \dot{L} \qquad L(t) = D - h(t)[D/d - 1]$$ (3-11)

The time, t=0, is the time at which the heat is applied suddenly to the surface. Time $t=t_1$ is the time at which the surface reaches the temperature T^*, the temperature at which intumescence begins. The front then begins to move to the left while the free surface moves to the right, as shown in Figure 3-2. Finally, at time $t=t_2$, the front reaches the substrate—intumescence is complete, and the only thing protecting the substrate from the external heat source is the char, Figure 3-3.
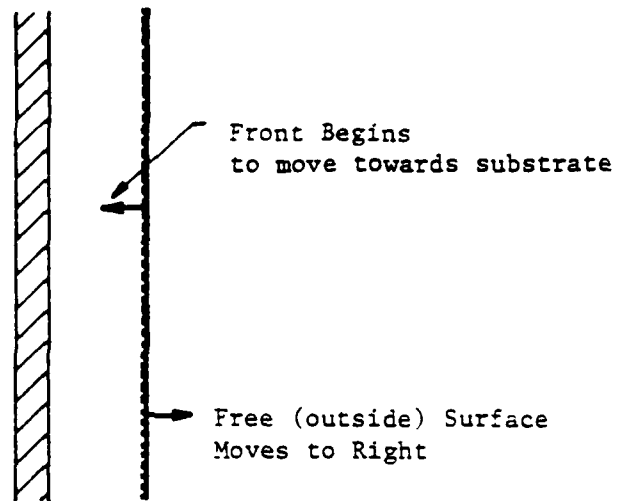
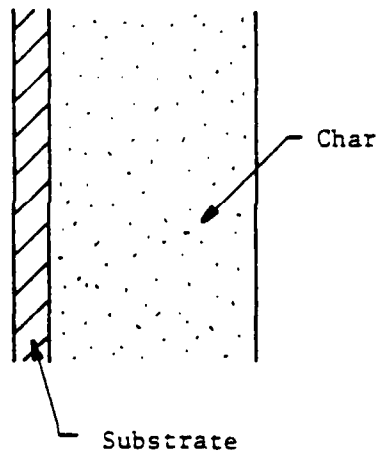Figure 3-2.   Schematic of Frontal Model, $t=t_1$

Figure 3-3.   Intumescence Complete, $t=t_2$

This discussion essentially describes the physical model; Appendix B goes into the details of the equations, nondimensionalization of the equations, and the procedure followed for obtaining solutions. We shall now discuss some of the results of the model, and the insights it provides.

3.3 Discussion of Results

The results of the frontal model can be divided into three time phases: the preheat phase, the intumescence phase, and the char phase. In the preheat phase, the virgin material is being heated by conduction until the surface reaches T^*. During the preheat phase, the analysis shows that the temperature within the coating increases linearly with time:

$$\frac{T}{T^*} \sim \frac{E}{\alpha}\tau + \frac{1}{2}E\left(\frac{x}{d}\right)^2 + \frac{T_o}{T^*} - \frac{1}{6}E + o(1) \tag{3-12}$$

$$\alpha = \frac{\rho_o k_f}{\rho_f k_o} \qquad \tau = \frac{tk_f}{\rho_f C_p d^2} \qquad E = \frac{\dot{q}_o d}{k_o T^*} \tag{3-13}$$

where $\dot{q}_o$ is the heat flux applied at the surface. At $x=0$, that is, the substrate coating interface, the temperature is given by:

$$\frac{T}{T^*} \sim \frac{E}{\alpha}\tau + \frac{T_o}{T^*} - \frac{1}{6}E + o(1) \tag{3-14}$$

Substituting Equations (3-13) into (3-14) gives:

$$T \sim T_o + \frac{\dot{q}_o}{\rho_o C_p d}\left(t - \frac{d^2\rho_o C_p}{6k_o}\right) = T_o + \frac{\dot{q}_o(t-t_o)}{\rho_o C_p d} \tag{3-15}$$

where t_o $(= d^2\rho_o C_p/6k_o)$ is associated with the heating at short times. Equations (3-12) through (3-15) are valid only for "large" times, where large can be approximated by $t > t_o$, which is of the order of 0.2 seconds for the NASA borax formulation.

When the surface temperature reaches T^*, intumescence begins and the second phase of the solution has begun. The time intumescence begins can be obtained from Equation (3-12) by inserting T^* for T and the coating thickness d for x:

$$t_1 - \frac{\rho_o C_p d}{\dot{q}_o} \left[T^* - T_o - \dot{q}_o d/3k_o \right] \tag{3-16}$$

For the NASA borax formulation, t_1 is on the order of 2.5 seconds.

Once time t_1 is reached the coating begins to expand and the "tumescent front" moves toward the substrate. Figure 3-4 is representative of the temperature-time history of the substrate coating interface. Note the plateau or leveling off of the temperature in Figure 3-4. The interpretation of this interesting feature predicted by the Frontal Model is as follows. The substrate is heating with time; however, the heat conducted to the substrate is limited because the temperature of the front is "clamped" at T^*. The heat flux to the substrate can increase with time since the distance between the front and the substrate is decreasing as the front moves toward the substrate. However, the substrate is shielded effectively from the high temperature of the external heat source which limits the heat flux until the front reaches the substrate. To be sure, the time it takes for the front to reach the substrate is dependent on the applied heat flux at the external surface and the effectiveness of the intervening char, but the substrate cannot rise in temperature past T^* until the front reaches the substrate. The time duration or length of the plateau is dependent on the external heat flux and the quantity of heat absorbed via endothermic processes [Q in Equation (3-7)] at the front. For example, if the endothermic process associated with the release of the blowing agent is not as large then the plateau will have a shorter time duration, Figure 3-5. It is interesting to note that even if no endothermic process is accounted for in the model (more strictly speaking, the applied heat flux is so large that the endothermic process is negligible in comparison), that so long as the front has a temperature T^* and the jump conditions exist, then a plateau still appears, though the time duration of the plateau is very short.

The time it takes for the front to reach the substrate depends upon the velocity of the front, $\dot{h}$, which changes with position; $\dot{h}$ has its largest value at the moment the surface begins to intumesce, and its smallest value the moment the front reaches the substrate. As char

$$\frac{T-T_o}{T^*-T_o}$$

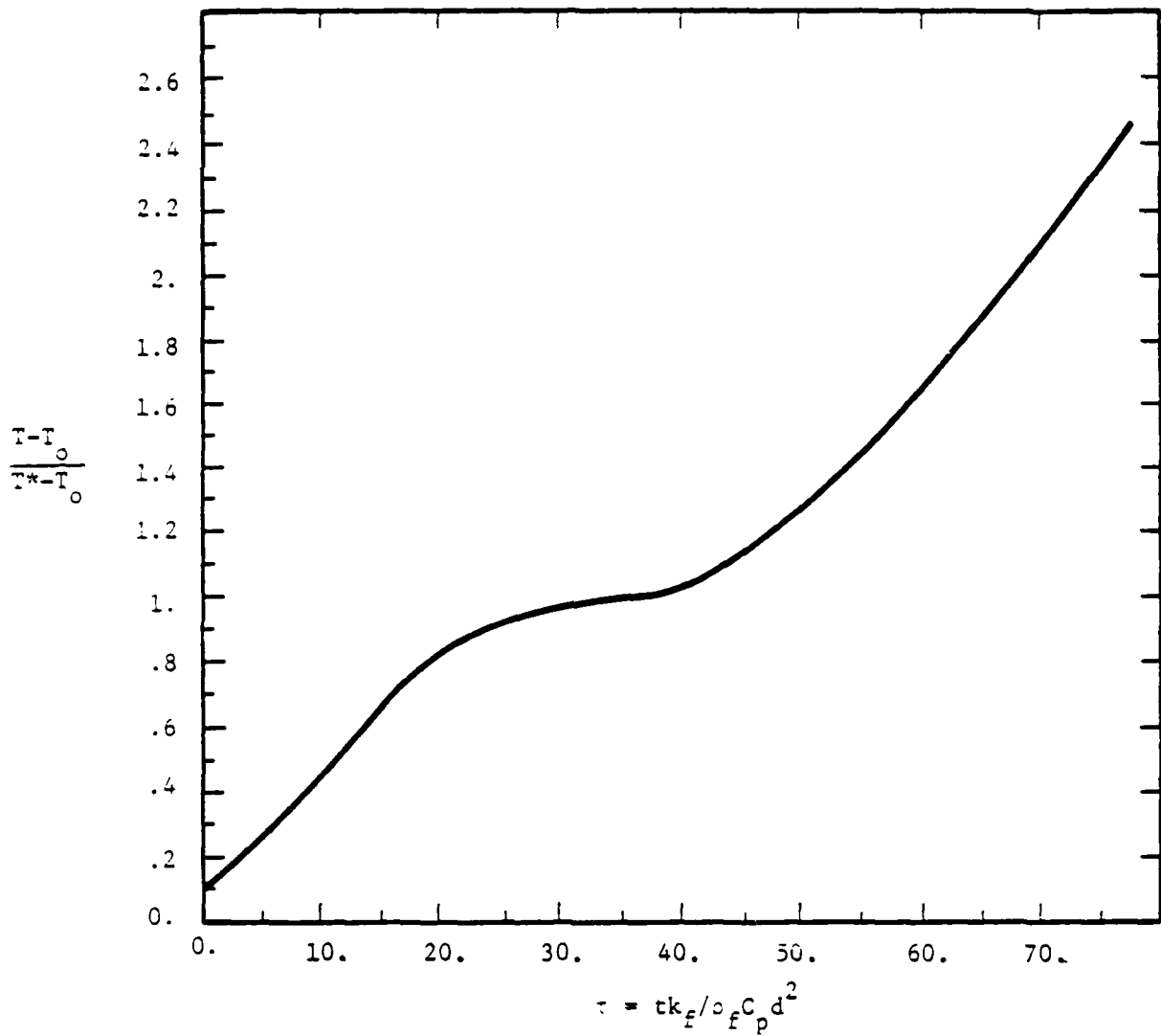$$\tau = tk_f/\rho_f C_p d^2$$

Figure 3-4. Model Prediction of Substrate Thermal Response

intervenes between the surface and the front, the velocity of the front can slow. Indeed, the slower the front moves toward the substrate, the more evident the plateau in Figures 3-4 or 3-5. If a char does not form between the surface and front, that is, the char ablates away, the front will see a larger heat flux than if there is an intervening char; the front would reach the substrate in a much shorter time, resulting in a short plateau.

It is quite evident from inspection of the temperature-time history when the front reaches the substrate. A sudden change in slope occurs and the temperature begins to rise rapidly. When the front reaches the substrate, intumescence is over and the coating material is now all char and fully expanded; the final phase, or char phase, now has begun. Once again the analytic solution, similar to Equation (3-12) shows that the substrate will increase in temperature linearly with time:

$$\frac{T}{T^*} \sim \frac{k_o d}{k_f D} E \ (\tau - \tau_2) + \frac{Dk_o}{dk_f} \frac{E}{2} \left(\frac{x}{d}\right)^2 + 1 + o(1) \tag{3-17}$$

where E and τ are defined by Equations (3-13). At the substrate coating interface, $x=0$, the temperature is given by:

$$T \sim T^* + \frac{\dot{q}_o (t-t_2)}{\rho_f C_p D} \tag{3-18}$$

Note that Equation (3-18) looks very similar to Equation (3-15) with the main difference being the denominators of the second term. $D\rho_f$ and $d\rho_o$ are, respectively, the mass per unit area of the char and the virgin material. Because of pyrolization and outgassing, the final mass is always less than the initial mass. Thus, the slope after intumescence will be steeper than before intumescence. That is, if $D\rho_f = d\rho_o$, the slopes before intumescence begins, and after intumescence is completed, would be the same. (It has been assumed that the specific heat per unit mass has changed very little between pre- and post-intumescence. The analysis could easily be modified to account for a "jump" in specific heat.) The model assumes a constant heat flux at the surface. In reality, the surface heats up and reaches a quasi-steady state temperature
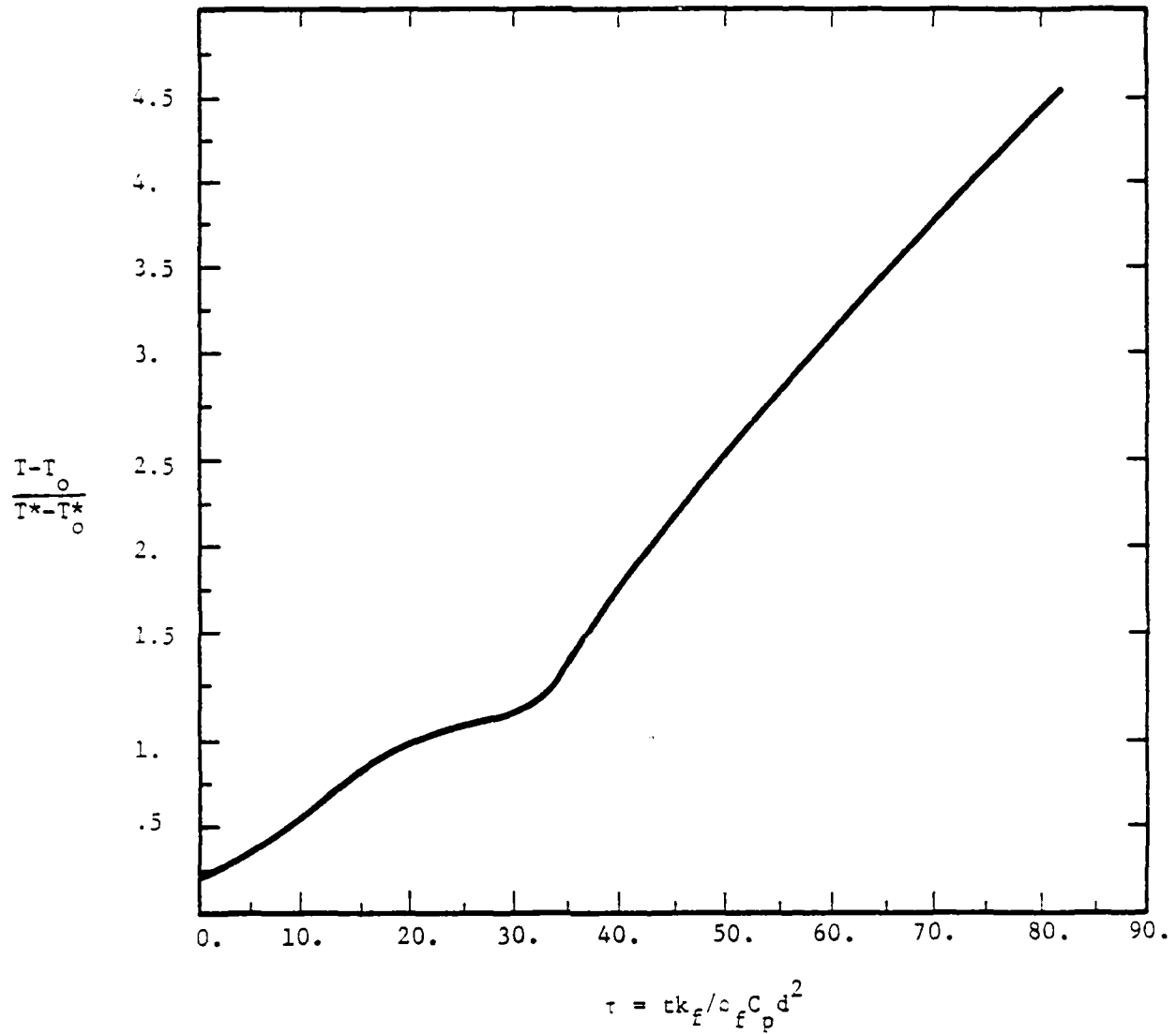
$$\tau = tk_f/c_f C_p d^2$$

Figure 3-5. Model Prediction of Substrate Thermal Response - Large Endotherm

which limits the heat flux absorbed. This eventually results in the tem-
perature-time curve approaching an asymptotic temperature which is near
an effective flame temperature. Thus, the constant heat flux approxima-
tion is quite valid until the substrate reaches a significant fraction
of the effective flame temperature.

The curves of Figures 3-4 and 3-5 were computed using values for
density, specific heat, thermal conductivity, and initial and final
coating thicknesses from the NASA borax formulation discussed in Section
2 and modeled in Reference 1. In particular:

$$\rho_o = 1.49 \ g/cm^3 \qquad\qquad \rho_f = .11 \ g/cm^3$$
$$C_p \sim .2 \ cal/g^{\circ}C$$
$$k_o = 5.5 \times 10^{-3} \ cal/cm\text{-}s\text{-}^{\circ}C \qquad k_f = 2.0 \times 10^{-3} \ cal/cm\text{-}s\text{-}^{\circ}C$$
$$d = .0965 \ cm \qquad\qquad D/d = 4.5$$

Thus, $\rho_f D = 0.05 < \rho_o d = .14$; hence, we would expect the slope of the
temperature time curves, Figures 3-4 and 3-5, to be greater after intu-
mescence. The differences in the two figures is the "size" of endotherm
at the front. As already stated, the larger the endotherm or heat sink
at the front, the more heat can be absorbed at the front, the slower the
front moves toward the substrate, and the longer in duration the plateau.

3.4 Comparison of Model Predictions with Experimental Results

We shall now compare model predictions with experimental data. Fig-
ure 3-6 depicts the actual temperature-time histories of several of the
intumescent systems tested in this program. Notice the distinct plateau
in several of the curves (these curves will be discussed in detail in
the next section). The model predicts distinct plateaux, in excellent
agreement with experimental results, and gives a physical basis for these
plateaux. While Anderson and Wauters [1] correctly deduced the physical
basis for these plateaux, it is now much clearer understood because of
the simplicity of the Frontal Model. Also note that the slope of the
post-intumescence phase is not always greater than pre-intumescence,
indicating either changes in specific heat and/or neglect of certain
physical phenomena (e.g., the absorbed heat flux is decreased as the sur-
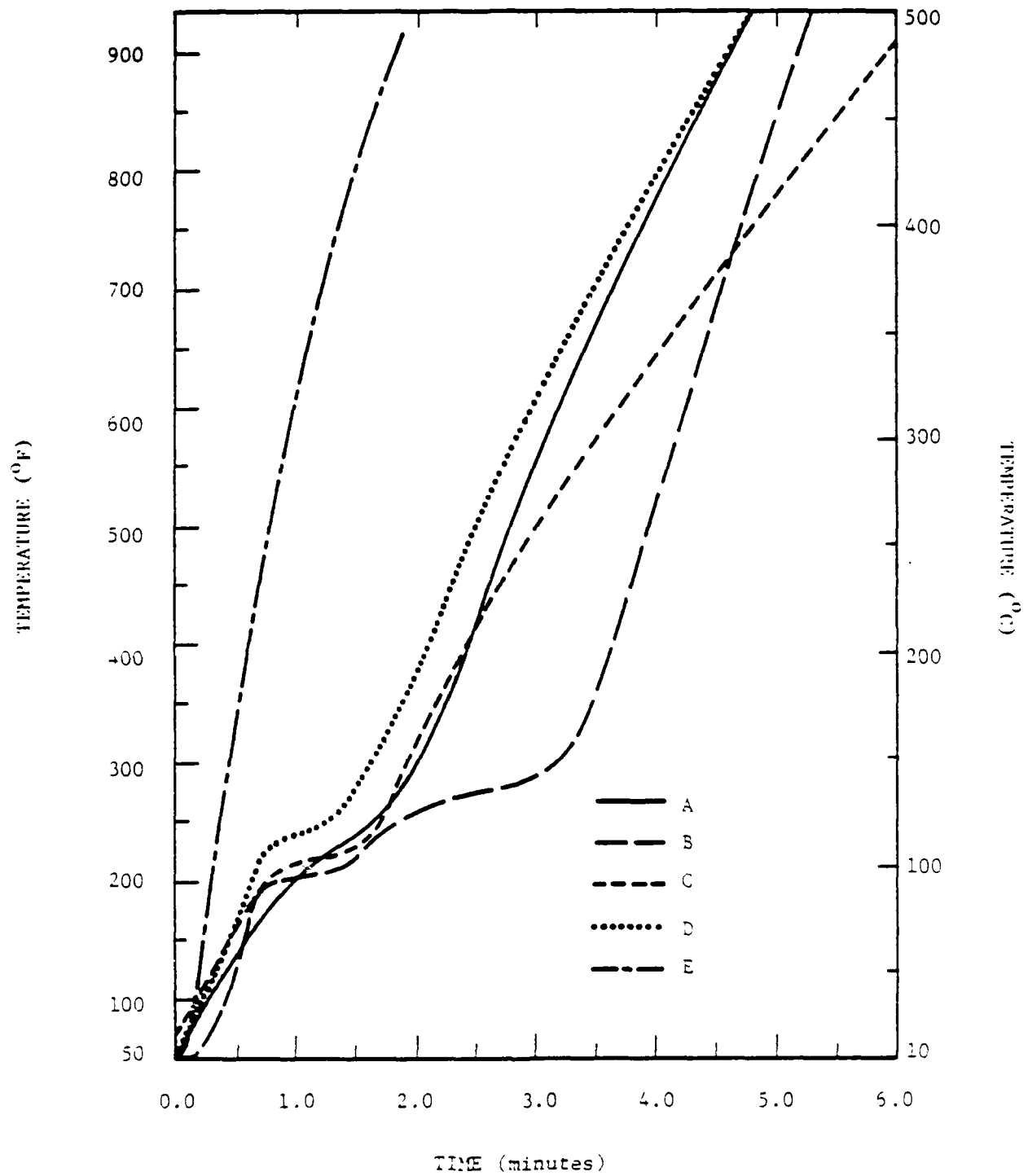face heats up since the thermal conductivity is smaller for the char,

-58-

Figure 3-6. Substrate Temperature-Time Histories of
Actual Intumescent Formulations

limiting the absorbed heat flux). Finally, for the most part, the experimental temperature-time curve is linear after the termination of the plateau, as predicted by Equation (3-18).

4.0 DISCUSSION OF EXPERIMENTAL RESULTS

It is difficult to assimilate the results of the experimental program because of the large number of tests which were conducted. One of the most useful ways to assess the experimental results is to compare visually the temperature-time histories of the various systems. In the figures which follow, an attempt has been made to compare different systems with approximately the same initial thickness. However, in view of the insights provided by the Frontal Model, it is more important to observe and compare the qualitative behavior of the different systems, i.e., the duration or extent of the intumescent plateau and other general behavioral characteristics of the thermal protection system. There was no need to reproduce all the temperature-time histories since many had the same qualitative behavior; differences in thermal performance could be attributed to initial thicknesses and these results are tabulated in the tables of Section 2. The borax-polysulfide/epoxy system (NASA formulation EX-1C-82), is also shown in the figures for comparison. Plate number 513 is the baseline NASA formulation. However, as already mentioned, variations in coating thicknesses more than mask small variations of concentration. Hence, for comparison purposes, in the following graphs an attempt was made to group different intumescent systems with approximately equal thicknesses. Plate 513 is used for comparison where coating thicknesses were approximately 1.7 mm, and plate 514 (also the NASA borax formulation but with a slight variation from the baseline in borax concentration) was used where coating thicknesses were approximately 2.1 mm. The following table provides a summary of the formulations compared in the figures:

Figure 4-1: Borax and Sodium Metasilicate (SMS)

Figure 4-2: SMS/Ammonium Phosphate and Aluminum Sulfate

Figure 4-3: Glauber's Salt

Figure 4-4: NASA Salt

Figure 4-5: Inert Fillers: Zinc Metaborate and Aluminum Hydroxide

Figure 4-6: Inert Filler: Syloid (SiO_2)
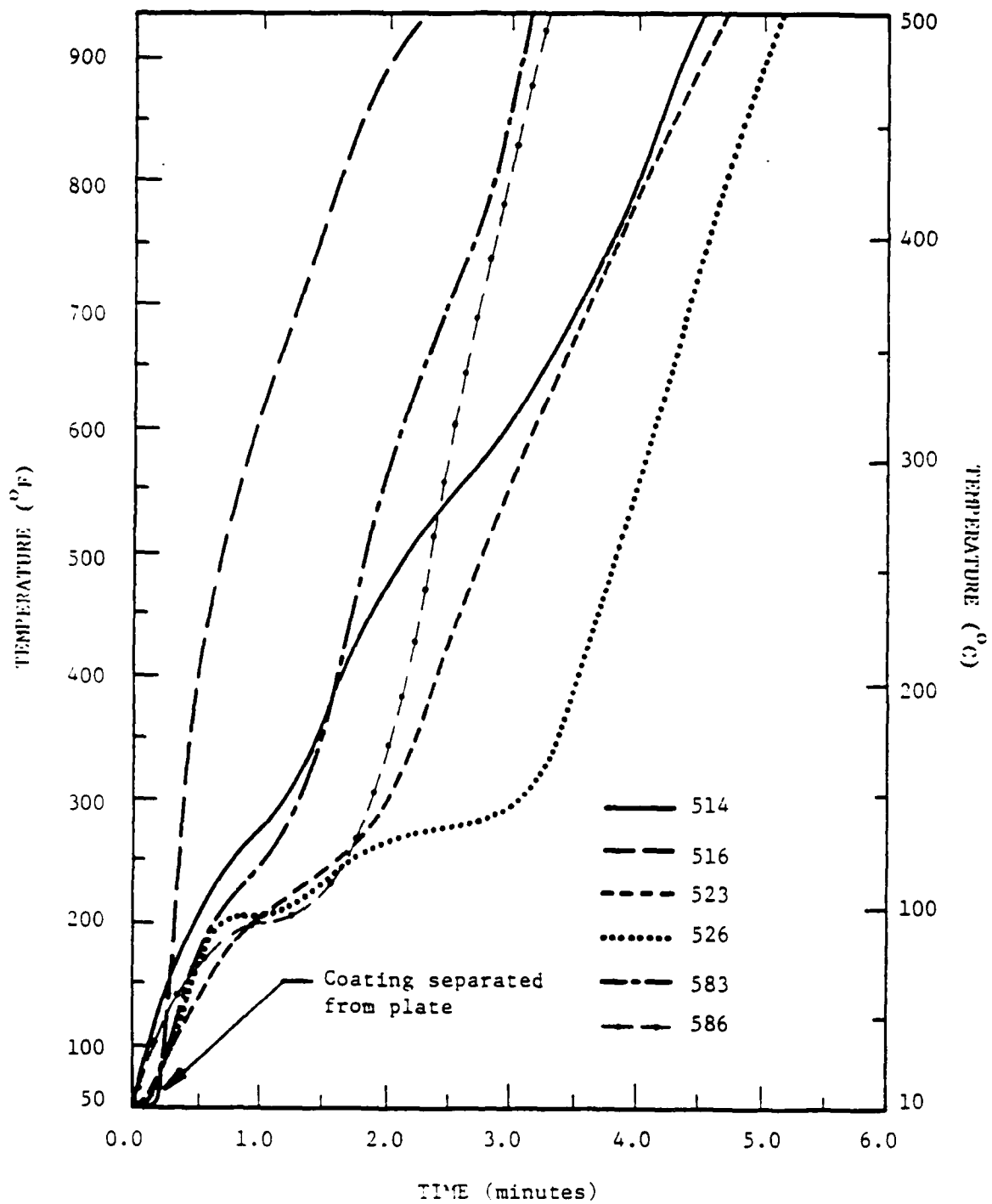
Figure 4-7: Borax-Neoprene with Different Solvents

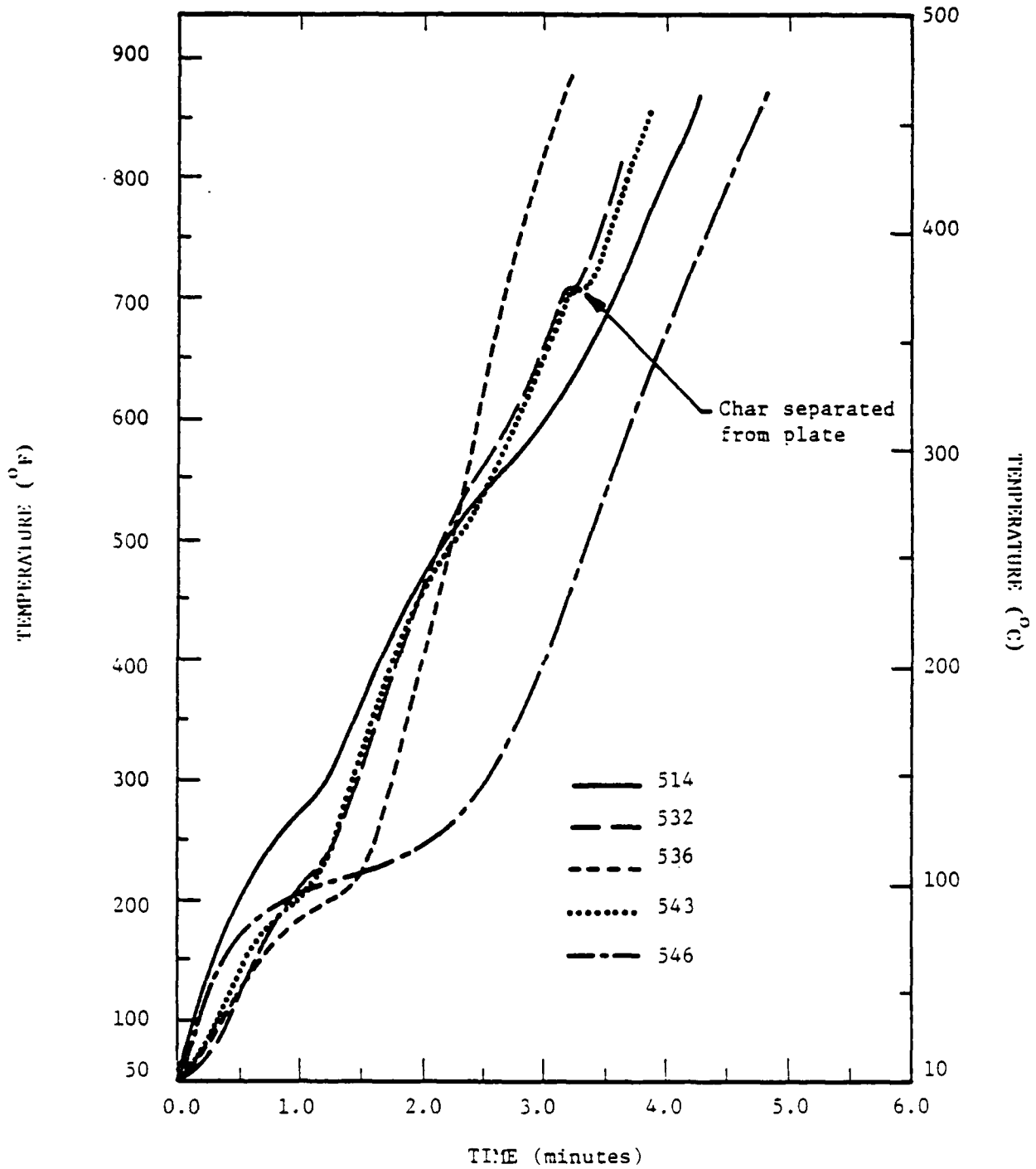Figure 4-1.   Borax and Sodium Metasilicate

Figure 4-2. Sodium Metasilicate/Ammonium Phosphate and
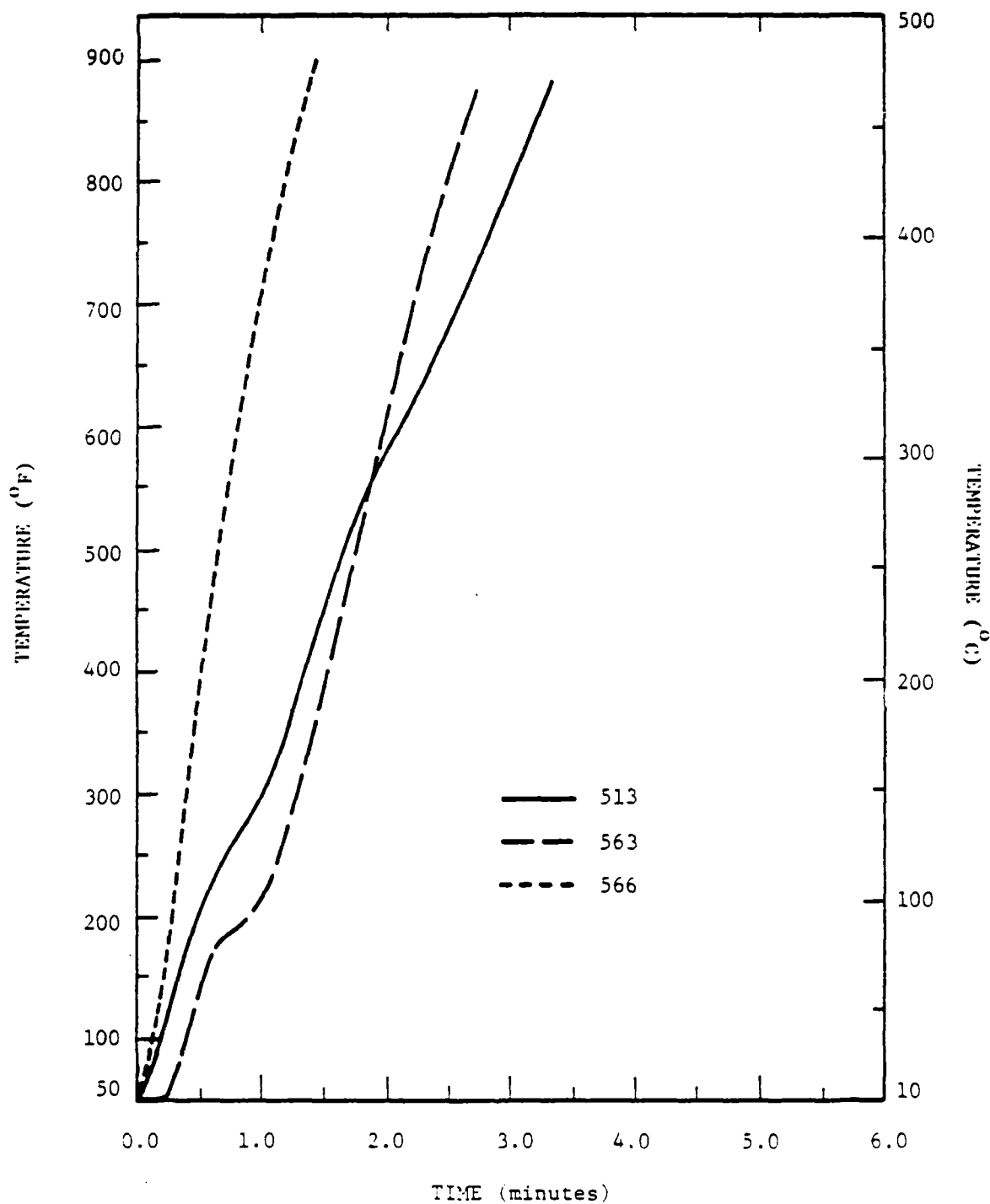Aluminum Sulfate

Figure 4-3. Glauber's Salt
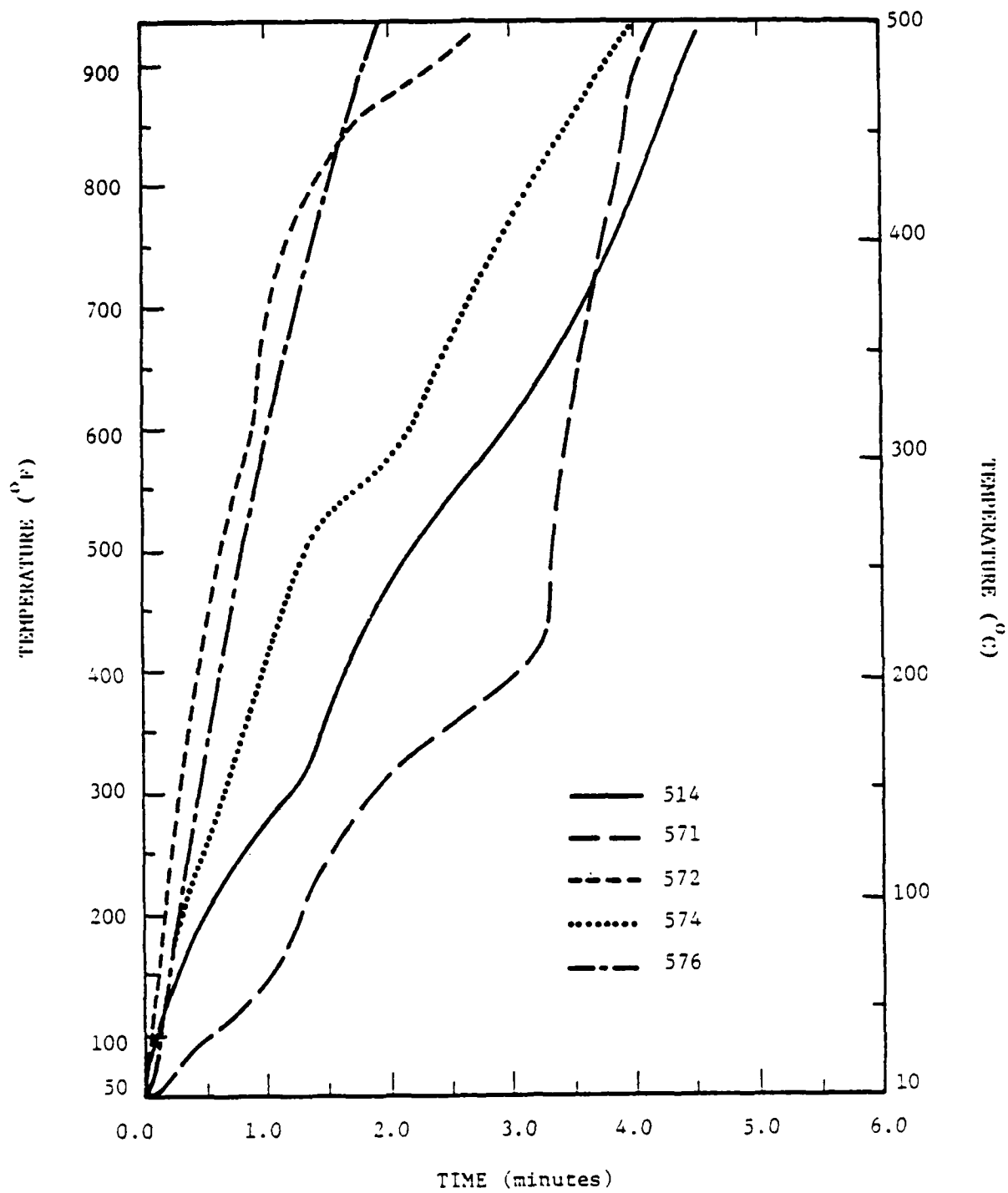
Figure 4-4. NASA Salt
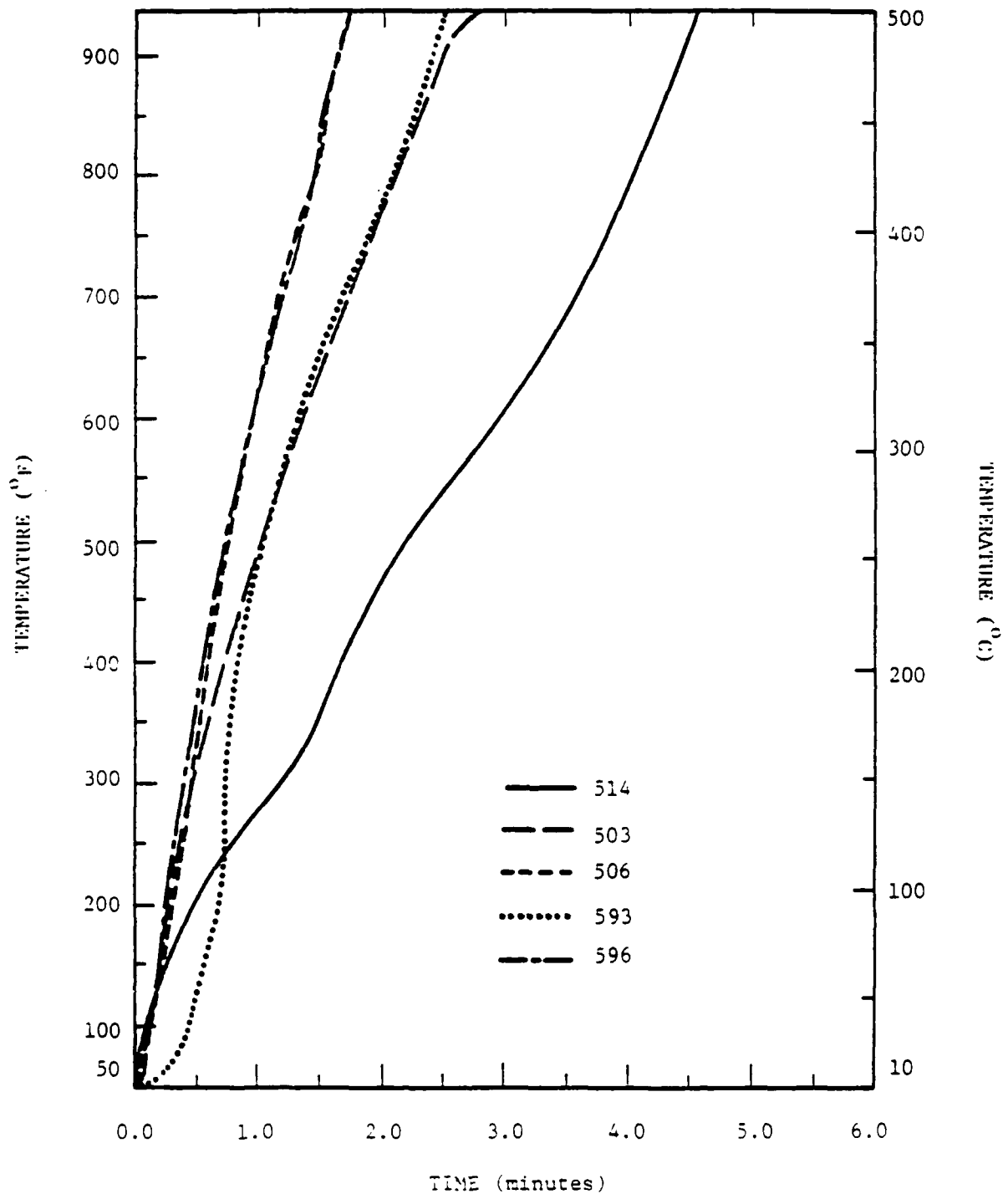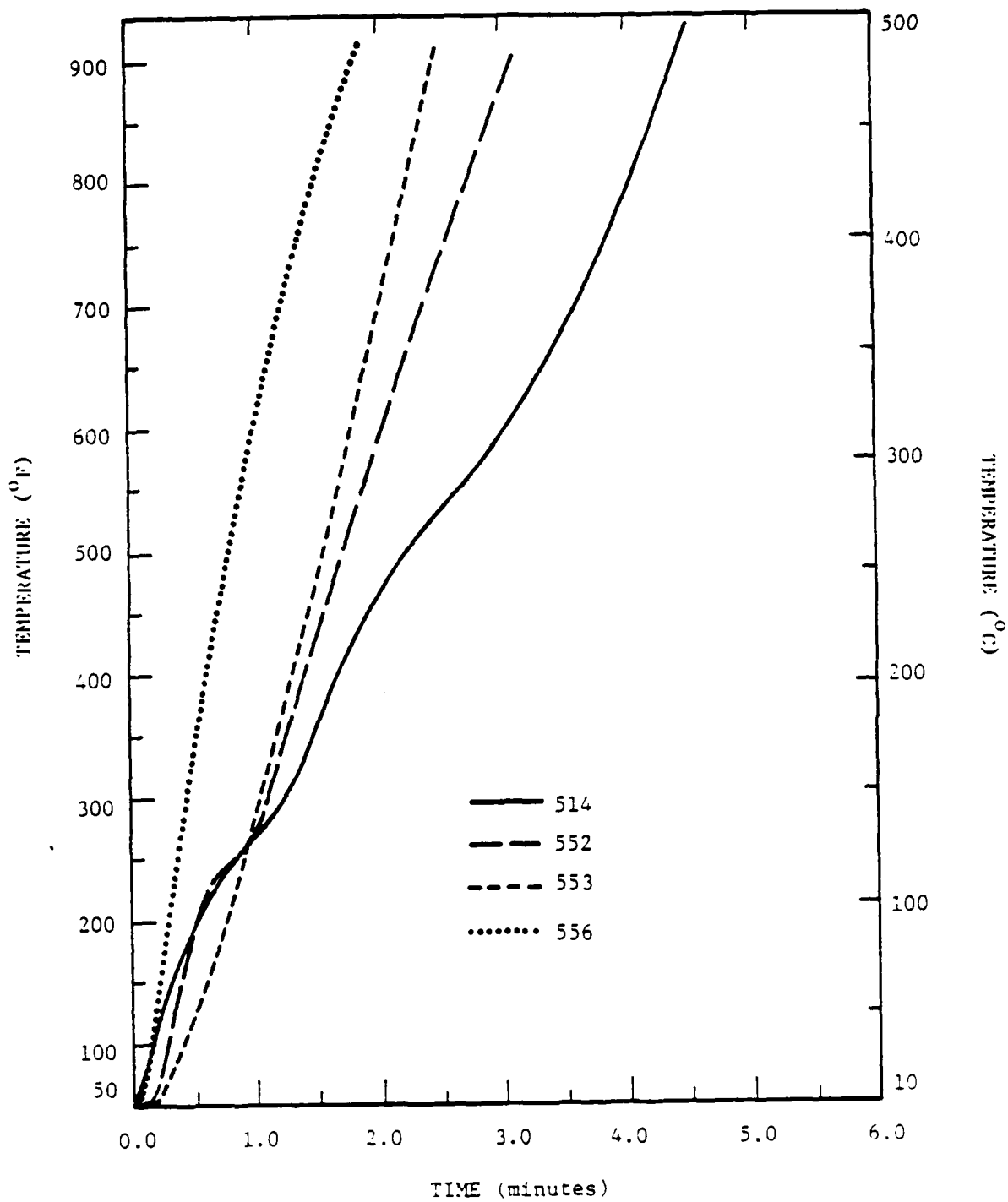
Figure 4-5. Inert Fillers: Zinc Metaborate and
Aluminum Hydroxide

Figure 4-6. Inert Fillers: Syloid (SiO$_2$)

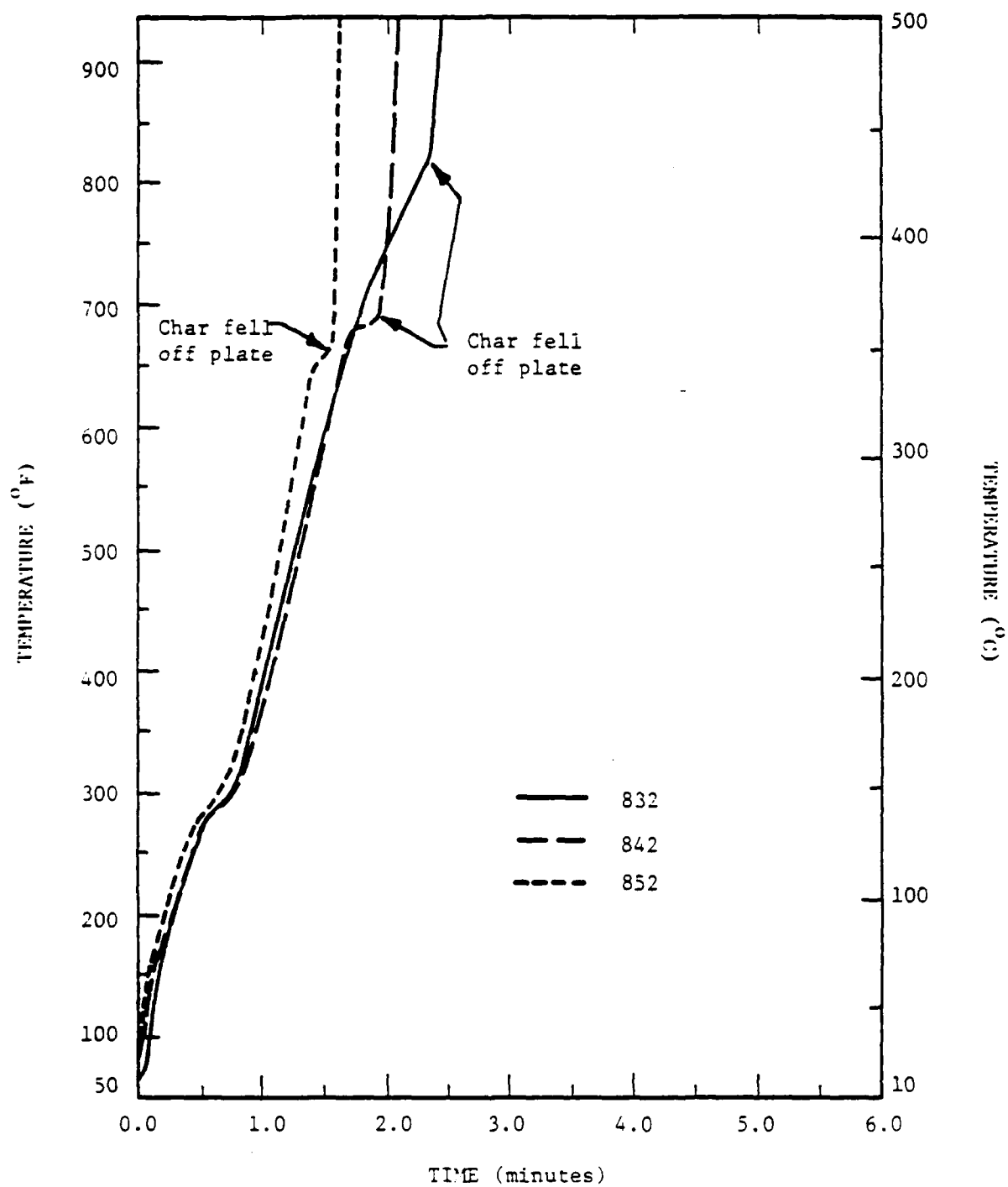Figure 4-7. Borax-Neoprene with Different Solvents

The following paragraphs will summarize some of the observations that can be made by analyzing these figures and the tables in Section 2.

Several observations can be made readily. Consistently, the sodium metasilicate-polysulfide/epoxy formulation had an adhesion problem, as did the borax-neoprene formulation. However, when borax and sodium metasilicate were combined as the filler, the resultant mixture appeared to work with both binders. Glauber's Salt was totally ineffective with both the polysulfide/epoxy and neoprene binders.

The NASA Salt showed tremendous variability, Figure 4-4. In some cases it outperformed the borax-polysulfide/epoxy formulation, while in other cases it performed extremely poorly. This is consistent with experimental observations of the NASA Salt in bomb cookoff tests. Nominally, the thermal performance of the NASA Salt is comparable to the borax-polysulfide/epoxy formulation. However, in some cookoff tests, the time-to-detonation of the warhead exceeded the nominal cookoff time; in other tests, cookoff occurred significantly less than the nominal value. This is probably due to the mechanism of intumescence; the NASA Salt relies on chemical reactions proceeding in a prescribed order to provide the blowing agent and intumescence; whereas, the majority of the other systems investigated in this study rely on the release of a chemically bound blowing agent such as water vapor. Because of the large variability of the NASA Salt with the polysulfide/epoxy binder, it is difficult to determine if the poor thermal performance (one test) with the neoprene binder is the consequence of not having the correct chemical formulation to achieve intumescence, or statistical variability.
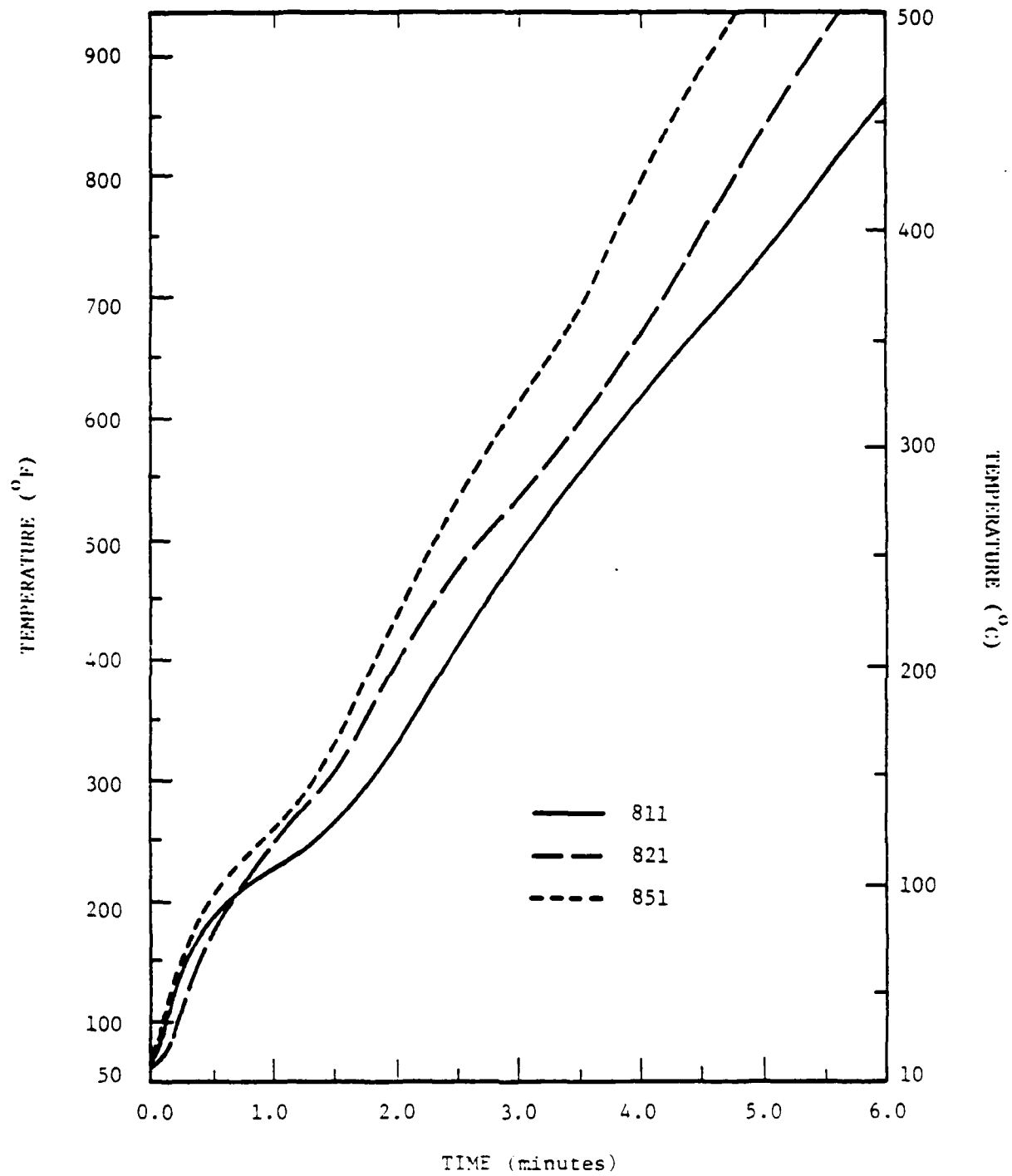
Figure 4-8. Borax-Polysulfide/Epoxy with Different Solvents
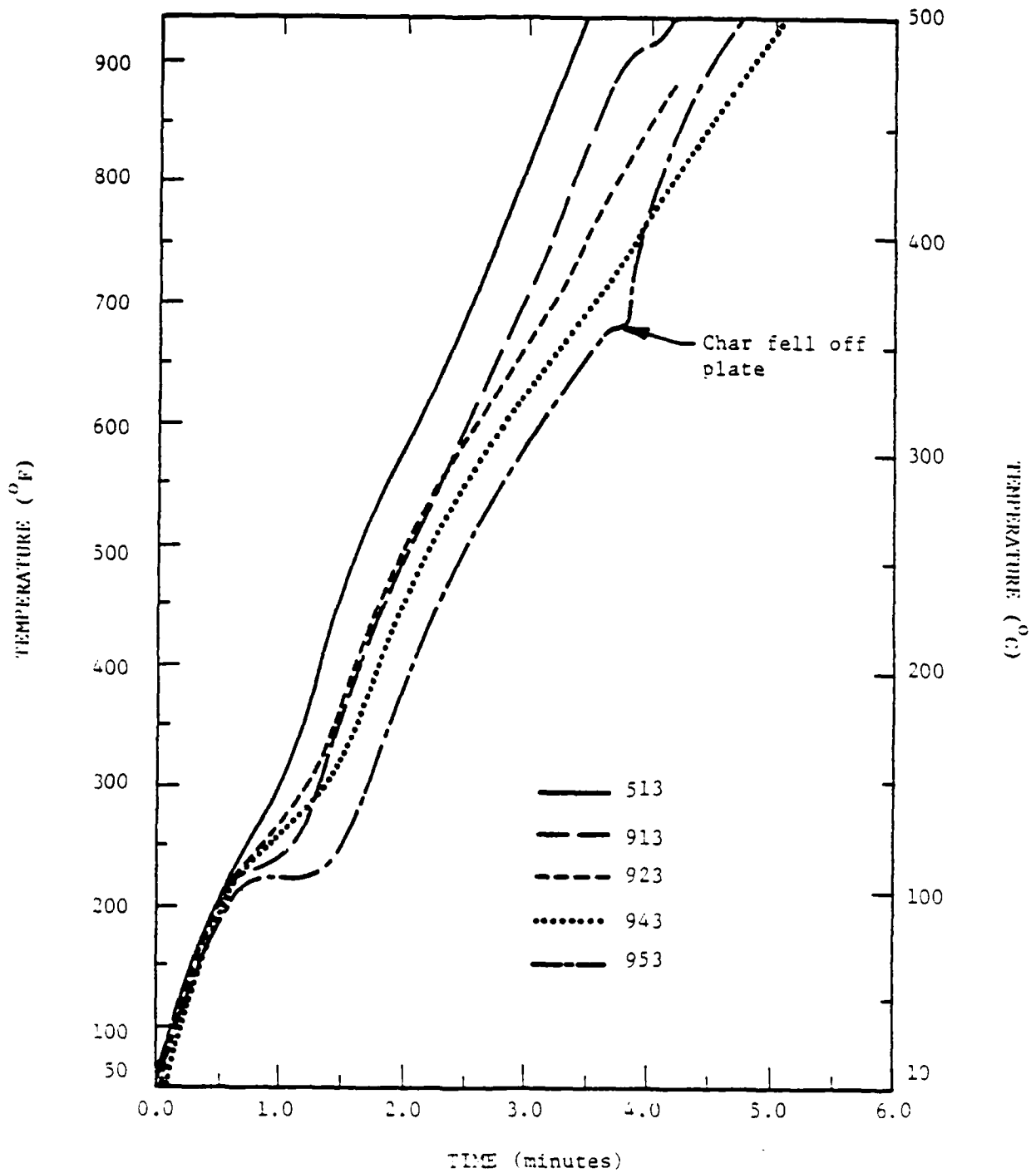
Figure 4-9. Concentration Variation of Glass Fiber in
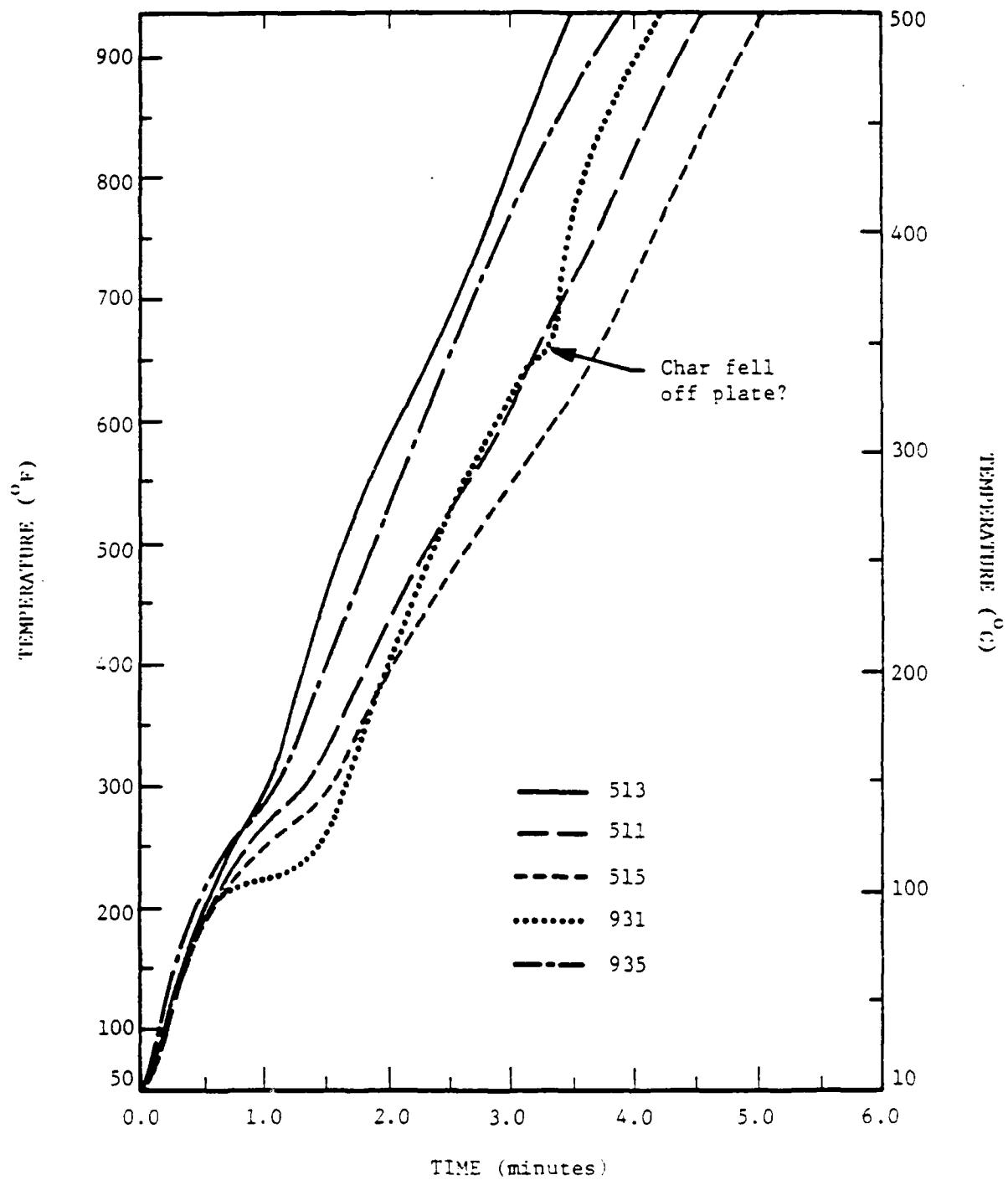Borax-Polysulfide/Epoxy Formulation

Figure 4-10. Concentration Variation of Borax in
Borax-Polysulfide/Epoxy Formulation
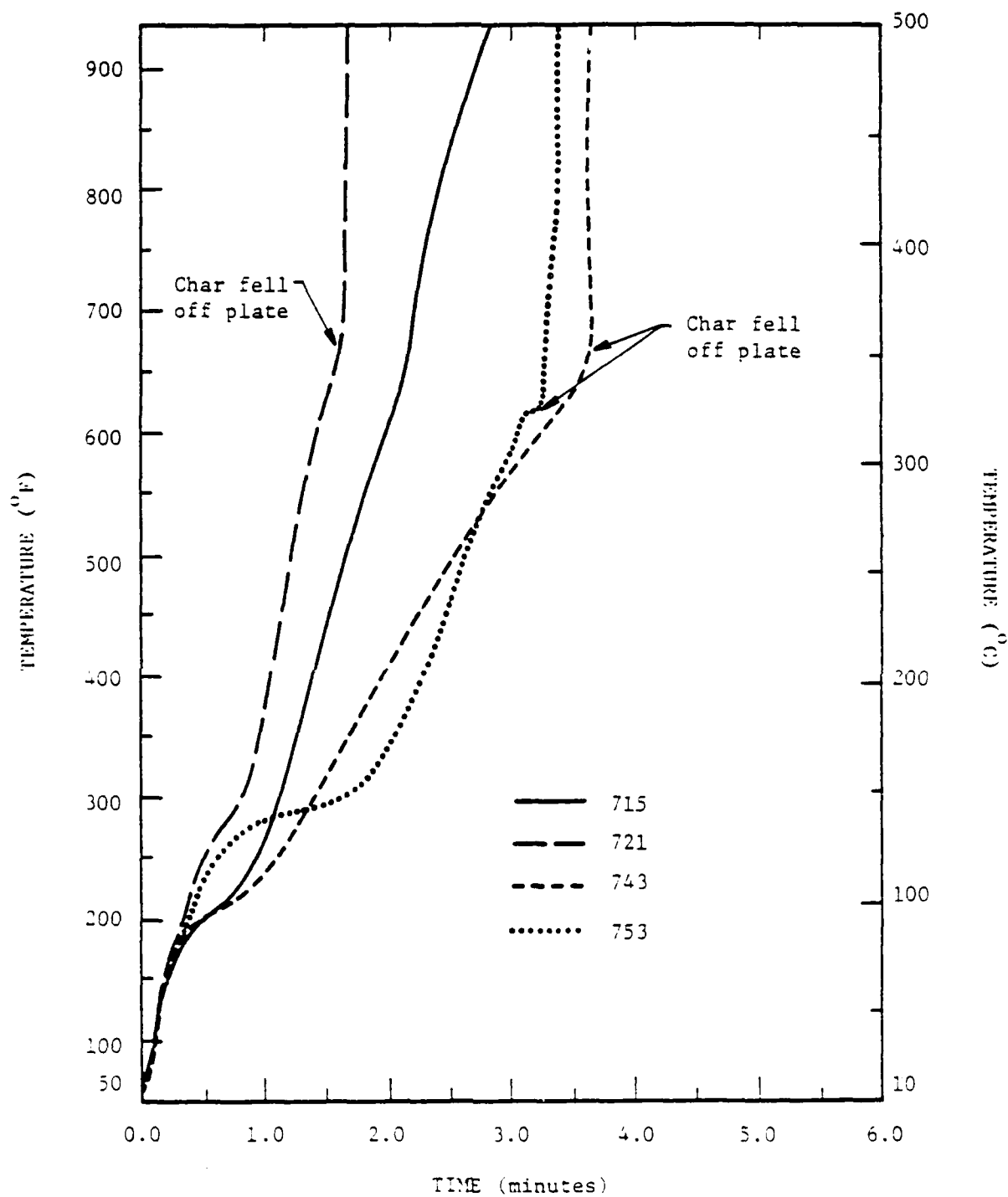(Bridging Agent: Glass Fiber)

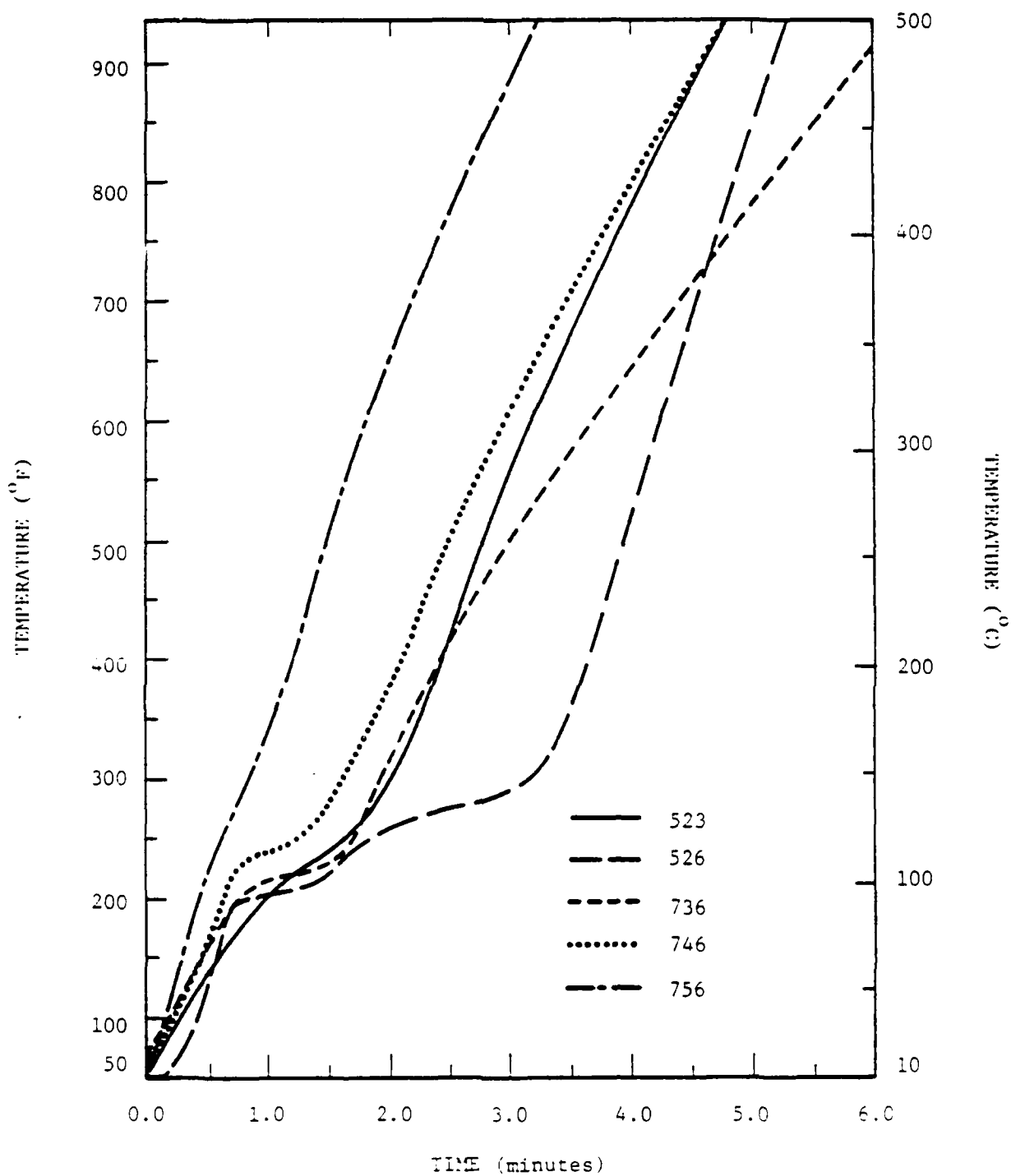Figure 4-11.   Borax with Different Binders

Figure 4-12. Sodium Metasilicate with Different Binders

The inert fillers, zinc metaborate, aluminum hydroxide, and silicon
dioxide (Syloid) do not, of course, exhibit intumescence. (The Syloid
may have had some adsorbed water which would have been liberated simi-
larly to the hydrated intumescent fillers. Aluminum hydroxide will
decompose to an aluminum oxide plus water, but this is a very slow
reaction which prevents it from acting as an effective blowing agent.)
And though these inert fillers do act as an insulator, they certainly
do not provide the thermal performance of an intumescent filler. It
should be noted that considerable mass loss and thermal expansion does
occur with these systems. The binders do decompose at the elevated
temperatures typical of a fuel fire. However, no intumescing front
forms and, as discussed in Section 3, a plateau does not develop in
the temperature-time history. Thus, it is assumed that the inherent
characteristic of an intumescent material is the formation of the
intumescent front with an associated temperature T^*; the formation of
the intumescent front is the key mechanism which allows the coating
system to act as an effective thermal insulator.

Three different solvents, methyl ethyl ketone, dichloromethane, and
toluene, were used to mix the constituents of the intumescent system
before application to a plate. Ostensibly, the thermal performance of
an intumescent system should be independent of the solvent used since the
solvents are volatile and will evaporate from the resulting mixture as it
cures. Basically, this supposition is confirmed in Figure 4-7, where the
borax-neoprene formulation shows very similar temperature-time histories
for the three solvents. However, the thermal response of the borax-poly-
sulfide/epoxy system shows some distinct differences, Figure 4-8, which
cannot be attributed solely to different thicknesses or slight differences
in the furnace's thermal environment. Typically, toluene has been used
as the solvent, and curve 851 is typical of previous experimental results.
The slight differences in the curves for the toluene and dichloromethane
solvated systems can be attributed to differences in initial coating thick-
nesses. But the MEK solvated formulation shows a much more distinct pla-
teau and better overall thermal performance. Toluene has the highest
affinity for polysulfide and MEK the lowest for the three solvents. The
solvent with the lowest solubility parameter would leave the least resi-

due of the solvent after curing. The ease of mixing the constituents, i.e., consistency, with respect to the three solvents was not recorded. Perhaps MEK provided a more homogeneous mixture of the constituents with an increase in thermal performance when it began to intumesce. These conjectures may or may not be the reason for the improved performance of using MEK as the solvent and a chemical analysis may be required to discern why one solvent appears superior to the others.

The variations of relative concentrations of the bridging agent to intumescent filler are shown in Figures 4-9 and 4-10. Generally, the interpretation of the experimental curves follows intuition: the bridging agent gives integrity to the char. When the quantity of bridging agent is decreased relative to the filler (curve 953), or the amount of filler is increased relative to the bridging agent (curve 931), intumescence is enhanced (a longer and flatter plateau), but the char is quite frangible and separates from the plate. The converse, more bridging agent relative to filler, or less filler relative to bridging agent retards intumescence. The absolute quantity of intumescent filler is important to the total amount of intumescence observed experimentally; thus, the curves in Figures 4-9 and 4-10 must be interpreted in light of the initial mass or thickness of the coating applied to the test plate.

The selection of an optimum fiber or bridging agent cannot be made from the limited number of tests performed. The variability of initial coating thickness makes it difficult to access the performance of the five bridging agents. It would appear, for the same relative concentrations, that the glass fiber provides more integrity to the char than graphite. The one graphite fiber test (621) appears to be completely out of line with several of the other tests (963, 973, 993) [reference tables in Section 2.0]. The mineral wool appears to be the least effective of the five fibers. To optimize thermal performance for a set of fibers would require more plate tests. The effect of different solvents also might be important in fiber performance as an effective bridging agent.

The last two figures are very interesting. Five binders were tried:
polysulfide/epoxy, neoprene, foundrez/epoxy, a flexible epoxy, and a
polyurethane resin. Figure 4-11 presents the temperature history cf
these binders with borax as the intumescent filler (borax was found
to be incompatible with foundrez). Figure 4-12 presents the temperature
history of the same binders with sodium metasilicate as the intumescing
filler. From examination of these figures it is very obvious that the
binder plays a dramatic role in intumescence. And it is considerably
more complicated than one of the binders being superior to the others.
For example, sodium metasilicate works best with neoprene, but the
intumescent front is virtually nonexistent with the polyurethane resin.
However, the borax-polyurethane resin system forms the most distinct
plateau of the borax-binder systems, and borax-neoprene the least.

Several observations can be made from Figures 4-11 and 4-12, along
with the tables in Section 2. The best thermal performance for ordnance
protection, that is, the longest plateau, had the smallest expansion
ratio, Table 27. What is unknown, however, is if the front surface of
the char for these systems ablated. There is indication that consider-
able ablation may have occurred in a number of the tests since it was
reported that none or very little of the char remained on a test plate.
Because of adhesion problems, and perhaps ablation, a definitive state-
ment on expansion ratio cannot be made; however, the limited information
from these tests, plus the insights from Section 3, would confirm Navy
experience [6] that large expansion ratios are not indicative or neces-
sary for good thermal performance of an intumescent system.

What causes the differences in the sodium metasilicate and borax
systems? Both fillers give up their bound water to form the blowing
agent. However, sodium metasilicate is more tenacious than borax in
trapping the water because of its high viscosity and low permeability.
The "tensile strength" of the sodium metasilicate far exceeds that
of borax, even in its viscoelastic state; hence, one expects that it
might not expand as greatly as borax in spite of the fact that the
blowing agent has a more difficult time percolating to the surface.
However, the most important aspect is that sodium metasilicate becomes

polymeric. The residual char of a borax-binder system must rely completely on the attributes of the binder to provide char integrity. Since neoprene alone forms a frangible char, the borax-neoprene system performed poorly. However, the dehydrated sodium metasilicate probably combined with the neoprene to form a char with excellent integrity. One observation is obvious, the selection of a binder has a dramatic effect on the resulting thermal performance of an intumescing filler.

An extremely important observation can be made with respect to Figures 4-11 and 4-12. The best intumescent system for protecting ordnance is the one with the longest, i.e., most distinct, plateau. Typically, the thermal performance of intumescent systems (as well as other thermal protective systems), as used by the Navy, is evaluated on the time it takes for an insulated test plate to reach $260^\circ C$ ($500^\circ F$), or the time to $260^\circ C$ per unit thickness of insulation. In protecting steel such as a steel I-beam supporting some structure, the time to $425^\circ C$ ($800^\circ F$) is used to evaluate thermal performance, a valid method of ranking an insulating system since the strength of steel begins to degrade rather substantially at temperatures in excess of $425^\circ C$. However, the Navy has recognized that explosives typically begin to undergo an irreversible exothermic reaction at temperatures on the order of $200^\circ C - 400^\circ C$. Thus, to prevent warhead cookoff, the explosive or propellant must be protected from the fire; hence, a long duration temperature plateau as depicted in Figures 4-11 and 4-12, all of which lie below $150^\circ C$ ($300^\circ F$) is desired.

5.0 SUMMARY AND CONCLUSIONS

A considerable number of test plates were coated with various intu-
mescent systems and exposed to a fire-type environment. The temperature-
time histories of the thermally protected substrates have been analyzed
and discussed. The hope that careful control of the percentages of the
various constituents would permit optimization of a particular formula-
tion was not realized. Variances in coating thicknesses more than
masked the small variations in the formulations. Though care was exer-
cised in application of the coatings, in hindsight, the coatings should
have been applied slightly thicker and then machined down to a uniform
thickness, as could be done by wet-sanding. Albeit that the experimental
testing did not provide the quantitative predictive capability desired,
the large and systematic variation of fillers, binders, and bridging
agents provided considerable insight to intumescent reaction mechanisms,
as well as some viable candidate intumescent systems for protecting
ordnance.

Providing considerable insight into intumescent reaction mechanisms
has been the development of a Frontal Model; the major assumption of
the Frontal Model is that the important physics of intumescence takes
place in a narrow zone which is relatively sensitive to temperature.
The Frontal Model then takes advantage of this assumption by approxi-
mating mathematically this pyrolization region, called "the front," as
infinitesimally thin and at a temperature $T*$. The heat equation is
applicable on both sides of the front (i.e., the virgin material side
and the char side) and the two regions (virgin material and char regions)
are connected by using jump conditions in the velocity, heat flux, and
mass (i.e., mass loss). With these assumptions, the Frontal Model pre-
dicts and explains a fundamental property of an intumescing system—
the formation of an isothermal front which moves from the free surface
to the substrate. As long as the isothermal front persists, the heat
transfer to the substrate is limited by the temperature gradient between
the front and substrate. In effect, the substrate is protected from
the higher temperatures of a fire by an intervening front that is char-
acterized by a temperature considerably lower than the flame temperature.

This limiting of the heat flux to the substrate manifests itself
in a decrease in the slope of the temperature-time history curve of the
substrate. If the front persists "long enough," then the temperature-
time history forms a plateau which is asymptotic to the temperature
of the front. Once the front reaches the substrate, then the substrate
again heats rather rapidly.

Analysis of the test data confirmed what the Navy has determined
from previous experimental programs. Large expansions are not necessary
(and certainly can be detrimental if the char becomes very frangible)
for good thermal performance of an intumescent system. Indeed, the most
promising intumescent system (sodium metasilicate as the filler and
neoprene as the binder) had the smallest expansion ratio of any system
tested. Inert, fire retardants such as silicon dioxide, zinc metaborate,
and aluminum hydroxide were the fillers in some of the systems tested;
charring and thermal expansion of the binder often resulted in consid-
erable mass loss and an expansion ratio greater than 2.0, and as high
as 8.76, yet these systems generally are not considered as intumescent
systems. Thus, a more precise definition of an intumescent system may
be one in which an *isothermal front forms* resulting in a plateau in the
temperature-time history of a substrate, as described in the paragraphs
above.

The important findings, not all of which can be explained, are
synopsized below:

- The selection of a binder plays a very crucial role on the
  resulting thermal performance of an intumescing filler; that
  is, the thermal performance, including adhesion, can be dra-
  matically altered by the selection of the binder.
- The NASA Salt demonstrated tremendous variability in thermal
  performance, perhaps in large part because it depends on
  chemical reactions proceeding in exactly the right sequence
  to achieve intumescence; all the other intumescent fillers
  examined in this study released a bound blowing agent (such
  as water). These results were consistent on similar tests.

- The solvent used in preparation of an intumescent formulation can sometimes affect the thermal performance of the intumescent system, as was evident by using methyl ethyl ketone instead of toluene in the borax-polysulfide/epoxy system; the thermal performance of other intumescing systems was independent of the solvent used.

- The trend noticed with bridging agents is that when the concentration of bridging agent is decreased relative to the intumescing filler, that intumescence (i.e., thermal performance) is enhanced, but that the char is more frangible; conversely, when the concentration of the bridging agent is increased relative to the filler, thermal performance is degraded.

- Large expansion ratios are not indicative or necessary for good thermal performance of an intumescent system.

- The Frontal Model predicts the formation of a plateau in the temperature-time history of a substrate; the plateau persists until an isothermal front, associated with the endothermic mass loss process and intumescence, reaches the substrate.

- The best intumescent system for protecting ordnance is the one with the longest, i.e., most distinct, plateau.

The last item in the above list should be discussed further. Thermal performance, as measured by the Navy (time to $500^{\circ}F$ or $1000^{\circ}F$ per unit initial thickness), or the measure used in this report (time to $800^{\circ}F$ per unit thickness), is probably not the best judge of thermal performance with respect to protecting ordnance from cookoff. Rather, it is more important to protect the propellant or explosive from reaching temperatures at which they become exponentially exothermic, leading to catastrophic rupture of a case or high order detonation. As seen in some of the intumescent systems tested in this program, the systems with the longest and most pronounced plateaux in their temperature-time history will provide more protection, i.e., longer times to cookoff.

6.0 RECOMMENDATIONS

This research program has resulted in a better fundamental under-
standing of the physics of intumescence. Though further research in the
physics of intumescence is warranted, it also is recognized that con-
siderable chemistry comes to play, for example, the role of the binder
in the efficacy of an intumescent filler. The chemist or chemical
engineer is essential to the development of a viable intumescent formu-
lation; however, the insights into the fundamental physical mechanisms
provided by the modeling serve to guide the chemist in the selection of
components which could enhance or suppress certain fundamental effects.
The modeling is beginning to provide those insights.

The physics of intumescing systems is better understood from this
and the previous study [1], but further work in understanding the thermal
protection provided by an intumescing system should be pursued. For
example, the Navy has recognized that expansion of the coating, in of
itself, is not the dominant heat protecting attribute of an intumescing
system, but further work in this area could explain better the role of
expansion. The one area which has been ignored to date in modeling
efforts is a fundamental understanding of the expansion process itself.
Further research should provide insights to such effects as ablation
of the char and perhaps why thermal performance, as measured by time
to a temperature divided by initial coating thickness, is dependent on
initial thickness. Since thermal performance as it is now defined does
depend on initial coating thickness, a procedure should be developed
for determining fundamental properties of an intumescent system, e.g.,
the thermal conductivity of the char, from the experimental data.

The previous paragraph discussed what might be fruitful in analytic
modeling efforts. Several of the intumescent systems formulated and
tested during the present study have potential for the Navy Cookoff
Program as alternate intumescent systems for application to ordnance.
In particular, sodium metasilicate with neoprene looks quite promising
from a thermal protection point of view because of the long plateau

evident in the temperature-time history of the metal substrate. This
formulation should be investigated further, with attention being given
to a number of other traits such as pot life, ease of applicability,
weathering characteristics, adhesion, etc., in addition to its thermal
characteristics.

6.0 REFERENCES

1. Anderson, Charles E. Jr. and Wauters, Donna K., "Intumescent Reaction Mechanisms: An Analytic Model," NADC-82211-60, Naval Air Development Center, Warminster, PA, May 1983.

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3. Anderson, Charles E. Jr. and Wauters, Donna K., "A Thermodynamic Heat Transfer Model for Intumescent Systems," International Journal of Engineering Science, in publication.

4. Pulley, D. F., "Intumescent Coatings," Symposium on Corrosion Control by Coatings, Lehigh University, Bethlehem, PA, Nov. 1978.

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6. Private communication with D. Pulley.

APPENDIX A

FORMULATIONS AND EXPERIMENTAL MATRICES

END

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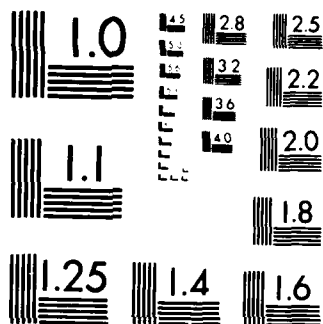
MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

APPENDIX A: FORMULATIONS AND EXPERIMENTAL MATRICES

A1.   Screening Studies

Preliminary screening studies were performed to determine which binders and intumescing/filler agents might be best suited for testing. For ease of operation, aluminum panels were used as a substrate for the coatings. An ideal coating thickness of approximately 1.40 mm (0.055 inches) was attempted, but system differences made for varied coating thickness. In some cases, adhesion to the aluminum was poor, but the experimental program incorporated steel plates instead of aluminum sheets. In the cases where a particular binder was being evaluated, sodium metasilicate and borax were used as the blowing agents.

The chief objective of these precursory tests was to determine which components would be most suitable and would warrant further study. As already stated, a 1.40 mm thick coating was the nominal thickness of an applied coating. After various representative coatings were cast, their qualitative thermal performance was evaluated as well as observational data on pot life, cure time, workability, flexibility, and adhesion. The coatings were applied to 7.62 cm by 7.62 cm by 1.02 mm (3 inches by 3 inches by 0.04 inches) aluminum panels. The cured specimens were subjected to heat by exposure to a Bunsen burner. Edges of the coating were shielded by sodium silicate foam to protect them from flame wrap-around at the edges. A wing tip on the Bunsen burner was used to give an even burn across the sample face. A thermocouple was mounted on the rear surface of the aluminum to give a semi-quantitative measure of the thermal performance. The preliminary test results are given in Table A1. The results are reported on the basis of their critical components (resin binder and intumescing or inert filler) with comments about the overall performance of each coating. The thermocouple data have not been included since these readings were only used to qualitatively rank thermal performance and could be misleading if not used in the spirit of these precursory tests.

Table A1. Screening of Intumescent Formulations

Binder(s)	Intumescing Agents	Remarks
(1) Foundrez	SMS (Sodium Metasilicate)·5H$_2$O Borax (Sodium Tetraborate)·10H$_2$O	Foundrez, a phenolic novolac resin binder with good adhesion, moderate toxicity in uncured state due to methanol and free phenol. SMS, non-toxic and commercially available, melting point 72°C with resultant loss of water of hydration. System flexible. Good burning characteristics.
(2) Neoprene	SMS Borax	Neoprene, a polychloroprene elastomer resin, fair adhesion and excellent flexibility. Somewhat combustible but less than natural rubber. System bubbled upon burning. Good burn test.
(3) Sodium Silicate	SMS	Sodium silicate (waterglass) non-toxic and noncombustible. Incomplete setting, incomplete gelling.
(4) Sodium Silicate Latex	SMS	Latex, an aqueous suspension of a rubber-like organic polymer. Incomplete gelling of system.
(5) Dow 736 Epoxy	SMS Borax	Dow 736 a polyglycol di-epoxide resin. Slow curing, needs heat curing at 130°F.

Table A1. Screening of Intumescent Formulations (Continued)

(6) Foundrez Epon 828 Epoxy	SMS Borax	Epon 828 a bisephenol A-polymer-epichlorhydrin copolymer. Slow cure, good flame test, heat speeds up cure.
(7) Dow 736 Epoxy	SMS Borax Aluminum Trihydrate Al(OH)$_3$	Al(OH)$_3$ a flame retardant. Slow curing, needs heat curing at 130°F.
(8) Foundrez Neoprene	SMS Borax	Has good adhesion and flexibility. Bubbled upon heating but still looks good.
(9) Neoprene Copaltite	Borax SMS	Copaltite a phenolic resin of the resole variety. Coating melted away upon firing.
(10) Latex	SMS	Quick set, burning produces much smoke.
(11) Neoprene [Different Brand Than (3)]	SMS Borax	Flame test shows promise, good adhesion. Different solvent in neoprene.
(12) Sodium Silicate	SMS	Added large excess of hardener and system gelled but did not set.
(13) Dow 736 Epoxy	SMS Syloid 244	Syloid 244 an amorphous, very low density silica filler. Contained additional hardener but still needs heat for reasonable cure time.

Table A1. Screening of Intumescent Formulations (Continued)

(14) Sodium Silicate Latex	SMS Syloid 244	Gelled but did not set.
(15) Dow 736 Epoxy Dow 325 Epoxy	SMS Al(OH)$_3$ Syloid 244	Dow 325 a bisphenol A-epoxy with aliphatic glycidyl ether. Has good adhesion but is brittle.
(16) Epon 828 Epoxy	SMS	Has good adhesion but is brittle. Burn test good.
(17) Polysulfide Epon 828 Epoxy	Borax	Polysulfide an organic polymer containing sulfur. Odorous. Has good adhesion and flexibility. Burn test fair.
(18) Sodium Silicate	Al(OH)$_3$ Syloid 244	Recipe set up but was brittle. Fire test was poor.
(19) Epon 828 Epoxy Copaltite	Borax SMS	Has good flexibility and fair adhesion. Burn test good.
(20) Carbomastic 14	SMS	Carbomastic 14 a coal tar epoxy. Has workability, adhesion, and flexibility.
(21) Thermal Chem 10 Epoxy	SMS Borax	TC-10, a polyamine cured flexibilizer epoxy having excellent flexibility, fair adhesion, tears easily. Burn test good.

Table A1. Screening of Intumescent Formulations (Continued)

(22) Neoprene	SMS Ammonia Phosphate (NH$_4$)$_2$ HPO$_4$	Ammonia phosphate a common flame retardant. Excellent flexibility, fair adhesion, very little intumescence but a good fire barrier. Coating remained intact.
(23) Neoprene	SMS Sodium Borate	Sodium borate an anhydrous filler. Good workability. Fire test good.
(24) Neoprene	SMS Al(OH)$_3$	Al(OH)$_3$ inhibits SMS from intumescing. Fire test fair.
(25) Neoprene	SMS Zinc Borate	SMS intumesces while Zinc Borate inhibits fire on Neoprene. Fire test good.
(26) Neoprene	SMS NASA Salt	Fire test was fair. Salt smokes upon firing.
(27) Neoprene	SMS Glauber's Salt	Fire test fair.
(28) Neoprene	SMS Sodium Nitrate	Fire test fair. Hazardous, explosive.
(29) Neoprene	SMS	Fire test good.
(30) Neoprene	SMS SMS Anhydrous	No intumescence from SMS anhydrous. Fire test fair.

Table A1. Screening of Intumescent Formulations (Continued)

(31) Neoprene	SMS Sodium Silicate Hydrate (4:1)	Sodium silicate will have some intumescence. Fire test good.
(32) Neoprene	SMS Ammonium Oxalate Hydrate	Ammonium oxalate hydrate toxic. Fire test fair.
(33) Neoprene	SMS Ammonium Pentaborate	Ammonium pentaborate is a fire retardant and not an intumescing agent. Fire test good.
(34) Neoprene	SMS Sodium Oxalate	Sodium oxalate is toxic. Fire test good.
(35) Foundrez Epon 828	Borax SMS $(NH_4)_2 PO_4$	Fire test fair.
(36) PVC Solution	SMS Borax	Coating burned away.

A2.   Formulations Components

Individual components were evaluated on the basis of performance (Table A1), cost, and individuality. For example, a number of inert fillers and/or fire retardants were considered. However, only one of each was chosen for full parametric evaluations. The major components (binders and intumescing agents) were more closely scrutinized since they constitute the main reasons for success or failure of a coating formulation. The materials selected to comprise the components of various formulations are listed in Table A2. The open circles in Table A2 designate alternate materials which were tested in a formulation, but with no parametric variations in concentrations. Particular characteristics of the various components are given in Table A3. Candidate components besides those in Table A2 were considered (e.g., Table A1) but not selected. The reasons for their elimination are given in Table A4.

A3.   Experimental Matrices

Test matrices incorporating the chosen materials are given in Tables A5 through A9. An attempt has been made to generate a testing program that gives data suitable for coating modeling, furnish information on intumescent coatings that was heretofore unavailable, and generate data that will advance our understanding of intumescent reaction mechanisms.

Once the components to be used were selected, baseline formulations were established which could be modified successfully to fit the test matrix. [No attempt has been made to optimize a particular coating formulation in terms of pot life, curing time, workability, ease of application, etc. However, a lab notebook was kept which documented formulation preparation along with relevant comments.] The main emphasis during the baseline formulation was on the relative concentrations of the binders and filler since they most affect coating workability. To establish the baseline formulations, each of the resin systems with various fillers was cast onto aluminum sheet material till a recipe yielded a proper average workability.

Table A2. Formulations Components

<u>Binders</u>   <u>Fibers (Bridging Agents)</u>

● Polysulfide-Epoxy   ● Glass Flake
● Neoprene   ● Graphite
o Foundrez/Epoxy   ● Kevlar
o Flexible Epoxy   ● Metal Fiber (Steel Wool)
                                        ● Mineral Wool

<u>Fillers</u>

● Borax
● Sodium Metasilicate
● Ammonium Phosphate
● Aluminum Sulfate Hexadecahydrate
● Inert Filler (Powdered Silica)
● Glauber's Salt
● NASA Intumescent Salt
o Borax/Sodium Metasilicate
o Zinc Metaborate
o Aluminum Hydroxide

Table A3(a). Components Considered and Selected
BINDERS

Polysulfide/Epoxy:
This is a mixture of Epon 828, a bisphenol A-polyepichlorohydrin copolymer, and a Thiokol polysulfide to impart a degree of flexibility to the system. Component of formulation meeting specifications of MIL-C-81945A (AS).

Neoprene:
Neoprene is an elastomeric polymer, polychloroprene, that is combustible but is self-extinguishing because of its halogen content. It has good chemical resistance to many common chemicals.

Foundrez/Epoxy:
Foundrez is a thermosetting phenolic novolac resin of imparting integrity to an epoxy system that is being subjected to fire.

Flexible Epoxy:
This is any of a class of highly flexibilized epoxies that have good impact resistance and good adhesion when compared to the more flexible elastomers.

Aromatic Polyurethane Resin:
This is a liquid urethane elastomer called Adiprene L-100 manufactured by Dupont and cured with Hughson Chemicals M-200 curing agent.

Table A3(b). Components Considered and Selected
FIBERS (Bridging Agents)

Glass Fiber:

Glass fiber is used as a bridging agent in
resin binders and will also act as a heat
reflective surface. The fibers used have a
nominal length of 0.8 mm (1/32 in.).

Graphite:

Graphite fibers are in use due tr ___ heat
resistance and their fine micro   .cture that
makes them excellent bridging m   .rial.

Kevlar:

Kevlar is a polyaramid fiber with very great
toughness, high tensile strength, and high
energy absorptive properties.

Metal Fiber (Steel Wool):

Steel wool is a common additive to resins
when relatively thick, or large, fibers are
desirable. It has excellent mechanical
strength properties and it will be interest-
ing to see if the high thermal conductivity
is detrimental to the thermal protection pro-
vided by the coating.

Mineral Wool:

Mineral wool is a common insulative material
that seems suitable for this application when
used in the candidate binders. It has good
chemical and thermal resistance and should
provide adequate bridging strength.

Table A3(c). Components Considered and Selected
FILLERS/INTUMESCERS

Borax:
Sodium tetraborate decahydrate, $Na_2B_4O_7$.
$10H_2O$, an ideal blowing agent as it relates
to a fire environment since it loses its
abundant water during heating from 75 to
320^oC, the range at which many organic
resins soften. Components of formulation
meeting specifications of MIL-C-81945A (AS).

Sodium Metasilicate
Pentahydrate:
$Na_2SiO_3 \cdot 5H_2O$ is a non-toxic, noncombustible
silicate that melts at 72^oC and loses its
water of hydration which then becomes a blow-
ing agent.

Ammonium Phosphate:
$(NH_4)_2 HPO_2$ is a non-toxic chemical commonly
used in flame-proofing combustible materials.

Aluminum Sulfate
Hexadecahydrate:
$Al_2(SO_4)_3 \cdot 16H_2O$ has an abundance of water and
a low melting point of 87^oC. It is a good
blowing agent.

Inert Filler (Syloid 244):
SiO_2 is finely powdered silica of extremely
low bulk density.

Glauber's Salt:
Sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$,
melts at 33^oC, loses its water at 100^oC, and
is ideal for an intumescent blowing agent.

NASA Intumescent Salt:
Developed by NASA, it is an excellent blowing
agent but has almost no physical integrity
after it expands.

Borax/Sodium Metasilicate:
This combination makes a good system since
they are chemically compatible and expand at
similar heats.

Zinc Metaborate:
$3ZnO \cdot 2B_2O_3$ is a commercially available fire
retardant of low toxicity.

Aluminum Hydroxide:
$Al(OH)_3$ [Aluminum Trihydrate] is commonly
used as a fire retardant.

Table A4(a). Components Considered But Not Selected
BINDERS

Waterglass:

Waterglass is a sodium silicate compound. The one evaluated is the 3:22:1 SiO_2:Na_2O formulation. Since it contains a high percentage of water, it is subject to shrinking and cracking. It has very little flexibility and impact resistance. The char is somewhat friable.

PVC:

Evolves toxic hydrogen chloride (HCl) fumes upon burning. Its adhesion to metal is poor.

Table A4(b). Components Considered But Not Selected
FIBERS (Bridging Agents)

Refrasil:

Refrasil is a silicon dioxide fiber having excellent high-temperature resistance but is very expensive.

Mica:

Mica is a good choice for a thin intumescent coating but it is in the same functional category as glass flake. The glass flake is more reflective to heat so it is chosen over mica.

Table A4(c). Components Considered But Not Selected
FILLERS/INTUMESCERS

Sodium Metaborate:

The commercially available octahydrate is an
intumescing agent but would not chemically
appear to offer any advantages over other
systems. Since the scope of this program is
limited, it will be deleted in favor of a
fire retardant and inert filler.

Ammonium Nitrate:

Ammonium nitrate is potentially explosive.
Its decomposition is somewhat high at 210°C
and evolves nitrous oxide, a narcotic and
potential explosive, as the blowing agent.

Slate and Limestone Fillers:

For our purpose, these minerals are classi-
fied as inert. Since they are more expensive
than silica powder, the inert filler chosen,
and since glass fiber, a reflectant, is al-
ready included, they will be deleted.

Triphenyl Phosphite:

Triphenyl phosphite has a low melting point,
22 to 25°C, and the resulting oil could bleed
to the surface and catch on fire.

Table A5. Various Fillers of Different Concentration
(Binder and Fiber Constant)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	X	X	X	X	X	X	X			
+ 5%	X	X	X	X	X	X	X			
Formula	X[a]	X	X	X	X	X	X	X	X	X
- 5%	X	X	X	X	X	X	X			
-10%	X	X	X	X	X	X	X			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H$_2$O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	X[b]	X	X	X	X	X	X	X	X	X

TOTAL: 52 Plates

a,b Cast two extra plates for each, one thicker and one thinner than nominal coating thickness.

Table A6. Variation of Fibers
(Binder and Filler Constant)

Binder: Polysulfide/Epoxy
Filler: Borax
          Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	X	X	X	X	X
SMS	X	X	X	X	X

TOTAL: 10 Plates

Table A7. Variation of Binders of Different Concentration
(Fiber and Filler Constant)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	X	X			
+ 5%	X	X			
Formula	X	X	a	X	X
- 5%	X	X			
-10%	X	X			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	X	X	X	X	X

TOTAL: 17 Plates

a Borax is incompatible with Foundrez.

Table A8. Variation of Solvent
(Binder, Filler, and Fiber Constant)

Binder: Polysulfide/Epoxy
          Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	X	X	X
Neoprene	X	X	X

TOTAL: 6 Plates

Table A9. Variation of Fiber to Filler Concentration
(Binder Constant)

Binder: Polysulfide/Epoxy
Filler: Borax
         SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			X							
+10			X							
0	X	X	X	X	X	X	X	X	X	X
-10			X							
-20			X							
SMS										
+20			X							
+10			X							
0			X							
-10			X							
-20			X							

TOTAL: 19 Plates

Test panels were then prepared; two specimen plates were prepared for each formulation — one plate was tested, the duplicate plate was prepared in case a primary plate/coating was damaged and it was also available to verify anomalies if they appeared in the test results. The test panels were made of steel with nominal dimensions of 7.62 cm x 7.62 cm x 1.40 mm (3.0 in. x 3.0 in. x 0.055 in.). A 2.54 cm (1.0 in.) diameter disc was removed from the center of each panel; 1.59 mm (.0625 in.) was then shaved from the circumference and then the disc was cemented back in place with a high-temperature epoxy adhesive.

A procedure was developed whereby a fairly uniform plate-to-plate coating thickness could be achieved. A doctor blade leaves a naked film, and trying to compensate for the viscosity may leave too thick a coating. A mold was devised to resolve these problems. The mold was made from a 3.175 mm (0.125 in.) thick sheet of aluminum cut in an "L" shape. Placing two of these L-shaped panels around the test plate forms a 1.78 mm (0.070 in.) cavity that can be filled with the coating material and leveled with a screed. The mold was made sufficiently large such that two specimen plates (the primary and the duplicate) could be coated at the same time.

After the technique of casting the coatings was devised, the specimen plates were weighed and bare plate thicknesses measured. The specimen plate was then stamped with an identifier corresponding to a designated coating formulation. These plate identifiers were also used as test identification (ID) numbers; the test ID's, along with their respective location in the test matrices are given in Tables A10 through A14.

A4. Formulations

The formulations, by mass, are given in Tables A15 through A19. All masses are given in grams. The solvent for all formulations was methyl ethyl ketone (MEK) except where specifically noted. As already stated, no attempt was made to optimize a particular coating formulation in terms of pot life, curing time, workability, ease of application, thermal performance, etc.

Table A10. Various Fillers of Different Concentration: Test ID No.
(Binder and Fiber Constant)

Binder: Polysulfide/Epoxy
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	511	521	531	541	551	561	571			
+ 5%	512	522	532	542	552	562	572			
Formula	513[a]	523	533	543	553	563	573	503	593	503
- 5%	514	524	534	544	554	564	574			
-10%	515	525	535	545	555	565	575			

Binder: Neoprene
Fiber : Glass Fiber

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
Formula	516[b]	526	536	546	556	566	576	506	596	506

a,b Cast two extra plates for each, one thicker and one thinner than nominal coating thickness.
ID suffix is 'M' for more (thicker) coating; 'L' for less (thinner) coating [e.g., 513M, etc.]

Table A11. Variation of Fibers: Test ID No.
(Binder and Filler Constant)

Binder: Polysulfide/Epoxy
Filler: Borax
          Sodium Metasilicate (SMS)

	Glass Fiber	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	513	621	631	641	651
SMS	523	622	632	642	652

Table A12. Variation of Binders of Different Concentration: Test ID No.
(Fiber and Filler Constant)

Filler: Borax
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
+10%	711	721			
+ 5%	712	722			
Formula	513	516	a	743	753
- 5%	714	724			
-10%	715	725			

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber

	Polysulfide/ Epoxy	Neoprene	Foundrez/ Epoxy	Flexible Epoxy	Polyurethane Resin
Formula	523	526	736	746	756

---

a Borax is incompatible with Foundrez.

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Table A13. Variation of Solvent: Test ID No.
(Binder, Filler, and Fiber Constant)

Binder: Polysulfide/Epoxy
Neoprene
Filler: Borax
Fiber : Glass Fiber

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	811	821	851
Neoprene	832	842	852

Table A14. Variation of Fiber to Filler Concentration: Test ID No.
(Binder Constant)

Binder: Polysulfide/Epoxy
Filler: Borax
SMS
Fiber : Glass Fiber and Graphite

	Glass Fiber					Graphite				
Borax	+20	+10	0	-10	-20	+20	+10	0	-10	-20
+20			931							
+10			511							
0	913	923	513	943	953	963	973	621	993	903
-10			515							
-20			935							
SMS										
+20			936							
+10			521							
0			523							
-10			525							
-20			930							

Table A15. Various Fillers of Different Concentration: Formulations
(Binder and Fiber Constant)

Binder: Polysulfide/Epoxy[c]: 11.3g/13.2g
Fiber : Glass Fiber: 5.0g

	Borax	Sodium Metasilicate	SMS/ Ammonium Phosphate	Aluminum Sulfate 16 H_2O	Inert Filler (Syloid)	Glauber's Salt	NASA Salt	Borax/ SMS	Zinc Metaborate	Aluminum Hydroxide
+10%	30.8	49.5	30.8/7.7	33.0	4.4	33.0	24.2			
+ 5%	29.4	47.25	29.4/7.35	31.5	4.2	31.5	23.1			
Formula	28.0[a]	45.0	28.0/7.0	30.0	4.0	30.0	22.0	18.0/18.0	30.0	6.0
- 5%	26.6	42.75	26.6/6.65	28.5	3.8	28.5	20.9			
-10%	25.2	40.5	25.2/6.3	27.0	3.6	27.0	19.8			
				Binder: Neoprene: 25.0g Fiber : Glass Fiber: 5.0g						
Formula	50.0[b]	55.0	48.0/12.0	45.0	10.0	40.0[d]	25.0	25.0/25.0	42.0	7.0

a,b Cast two extra plates for each, one thicker and one thinner than nominal coating thickness.

c Epoxy: EPON 828 11.5g
          DMP 30   1.7g

d Toluene was used as solvent because of MEK incompatibility.

Table A16. Variation of Binders of Different Concentration: Formulations
(Fiber and Filler Constant)

Filler: Borax
Fiber : Glass Fiber: 5.0g

	Polysulfide/ Epoxy[a]	Neoprene	Foundrez/ Epoxy[b]	Flexible Epoxy[c]	Polyurethane Resin[d]
+10%	11.43/12.65/1.87	27.5			
+ 5%	11.86/12.08/1.78	26.25			
Formula	11.30/11.50/1.7	25.0	e	16.0/3.0/3.0	10.0/10.0
- 5%	10.74/10.92/1.62	23.75			
-10%	10.07/10.35/1.53	22.50			
Borax	28.0	50.0	e	40.0	60.0

Filler: Sodium Metasilicate (SMS)
Fiber : Glass Fiber: 5.0g

	Polysulfide/ Epoxy[a]	Neoprene	Foundrez/ Epoxy[b]	Flexible Epoxy[c]	Polyurethane Resin[d]
Formula	11.3/11.5/1.7	25.0	10.0/20.0/2.75	16.0/3.0/3.0	10.0/10.0
SMS	45.0	55.0	30.0	50.0	70.0

[a] Epoxy consists of EPON 828/DMP 30
[b] Epoxy consists of EPON 828/Shell "U" Hardener
[c] Epoxy consists of DOW 735 epoxy/DOW DEH 58 Hardener/Shell "U" Hardener
[d] Epoxy consists of Uniroyal adipiene L-100/M200 Hardener
[e] Borax is incompatible with Foundrez

Table A17. Variation of Fibers: Formulations
(Binder and Filler Constant)

Binder: Polysulfide/Epoxy[a]: 11.3g/13.2g
Filler: Borax: 28.0g
Sodium Metasilicate (SMS): 45.0g

	Glass Flake	Graphite Fiber	Kevlar Aramid	Steel Wool	Mineral Wool
Borax	5.0	2.5	0.2	5.0	0.2
SMS	5.0	2.5	0.2	5.0	0.2

---

[a] Epoxy: EPON 828 11.5g
DMP 30 1.7 g

Table A18. Variation of Solvent: Formulations
(Binder, Filler, and Fiber Constant)

Binder: Polysulfide/Epoxy[a]: 11.3g/13.2g   Neoprene   : 25.0g
Filler: Borax: 28.0g   Borax   : 50.0g
Fiber : Glass Fiber: 5.0g   Glass Fiber: 5.0g

	Methyl Ethyl Ketone (MEK)	Dichloromethane	Toluene
Polysulfide/Epoxy	1.0	3.0	3.0
Neoprene	1.0	3.0	3.0

---

[a] Epoxy: EPON 828 11.5g
DMP 30 1.7g

Table A19. Variation of Fiber to Filler Concentration: Formulations
(Binder Constant)

Binder: Polysulfide/Epoxy[a]: 11.3g/13.2g
Filler: Borax
         SMS
Fiber : Glass Fiber and Graphite

Glass Fiber[b]

Borax	+20	+10	0	-10	-20
+20			33.6/5.0		
+10			30.8/5.0		
0	28.0/6.0	28.0/5.5	28.0/5.0	28.0/4.5	28.0/4.0
-10			25.2/5.0		
-20			22.4/5.0		

SMS	+20	+10	0	-10	-20
+20			54.0/5.0		
+10			49.5/5.0		
0			45.0/5.0		
-10			40.5/5.0		
-20			36.0/5.0		

Graphite[b]

Borax	+20	+10	0	-10	-20
0	29.0/3.0	28.0/2.75	28.0/2.5	28.0/2.25	28.0/2.0

a Epoxy: EPON 828 11.5g
          DMP 30   1.7g
b Filler(g)/Fiber(g)

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However, the formulations were varied to obtain an average workability such that a formulation could be parametrically varied and still be easily applied to the sample coupons.

The actual formulations used for each system are given in the tables. For example, the sodium metasilicate-polysulfide/epoxy formulation (Plate 523) is given in Table A15. Forty-five grams of sodium metasilicate were mixed with 11.3g of polysulfide and 13.2g of epoxy (which consists of 11.5g of EPON 828 and 1.7g of DMP 30). The left-hand columns, +5%, +10%, etc., refer to an increase or decrease of the respective component. For example, for the same sodium metasilicate-polysulfide/epoxy system, +10% means 10% more, by weight, of sodium metasilicate, i.e., 45g + (10%)45g = 49.5g (reference Table A15). "Formula" essentially refers to the baseline formulation of NASA EX-1C-82, but with different constituents substituted, e.g., sodium meta-silicate for borax, etc. However, "Formula" does not mean exact substitution by weight since concentrations had to be varied to achieve an average workability.

Some problems of particular note occurred during formulation preparation. Glauber's Salt $Na_2SO_4 \cdot 10H_2O$ coagulated the methyl ethyl ketone (MEK) solvated neoprene, and isolated the neoprene. Toluene was used as an alternate solvent. The aluminum sulfate$\cdot 16H_2O$ inhibited (destroyed) the cure on the epoxy/polysulfide system. Low level heat ($110^\circ F$ for one week) did not aid the cure. The coating was very pliable, but the plates were included for testing. Borax, when added to the phenolic resin, foundrez, caused coagulation; these specimen plates could not be prepared.

All coated plates were cured at room temperature conditions except the aromatic urethane that was heated to $99^\circ C$ ($210^\circ F$) for six days, and the DOW 736 flexible epoxy system that was cured at $66^\circ C$ ($150^\circ F$) for 18 hours.

APPENDIX B

A FRONTAL MODEL FOR INTUMESCENT PAINTS

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A FRONTAL MODEL FOR INTUMESCENT PAINTS

B1. The Mathematical Model

We shall deal with a one-dimensional configuration. In due course all source terms, whether of mass, volume, or heat, will be taken to be delta functions, consistent with the frontal model, but our initial discussion will not make this restriction. Unlike the Lagrangian formulations of the earlier analyses, we shall adopt a purely Eulerian description.

Outgassing causes mass loss at a rate $\dot{g}$ so that the equation for mass conservation has the form

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = -\dot{g} \tag{B1}$$

where ρ is the density and u the velocity.

Consider an isolated mass of virgin material, and consider what happens as it is heated. The increase in temperature turns the paint into a viscoelastic fluid which gives off gas. The generation of this gas creates voids which become frozen into the material as it hardens, which it does as more of the gas is liberated. Thus, mass is lost, but at the same time the volume increases. Suppose V_0, m_0 are the initial volume and mass, $\Delta V = V - V_0$ is the increase in volume (positive) and $\Delta m = m_0 - m$ is the decrease in mass (also positive). For a given viscoelastic state, we would expect that there is a relationship between the mass loss and the volume increase, which leads to the model

$$\frac{\Delta V}{V_0} = f\left(\frac{\Delta m}{m_0}\right) \tag{B2}$$

It is not at all apparent what is a reasonable choice for the function f, but one possibility is

$$f(x) = Cx^N \tag{B3}$$

This is the choice made by Anderson and Wauters (1983). It is open to the criticism that the viscoelastic state varies throughout the coating, because of variations in temperature and mass loss, so that corresponding variations in the function f should be accounted for; but what form these variations should take is unknown.

In order to incorporate a law such as equation (B2) into a field equation, it is convenient to introduce the concept of Lagrangian mass. Consider the mass of a unit volume of virgin material—it has a value of ρ_0. We now follow all of the particles in this volume, deleting those that turn into gas. The total mass is m, and it decreases from the initial value ρ_0 due to outgassing. The volume of this material is V where

$$V = V_0 \left[1 + f\left(\frac{\Delta m}{m_0}\right) \right] \tag{B4}$$

and $V_0 = 1$, $m_0 = \rho_0$. Since, according to equation (B1), $\dot{g}$ is the rate of mass loss per unit volume, it follows that

$$\frac{dm}{dt} = -\dot{g}V$$

corresponding to

$$\frac{\partial m}{\partial t} + u\frac{\partial m}{\partial x} = -\dot{g} \left[1 + f\left(\frac{\Delta m}{m_0}\right) \right] \tag{B5}$$

Moreover, there is a relation between ρ and m, namely $m = \rho V$ so that

$$m = \rho \left[1 + f\left(\frac{\Delta m}{m_0}\right) \right] \tag{B6}$$

The only significant energy is thermal in nature, so the energy equation has the form

$$C_p \frac{\partial}{\partial t} (\rho T) + C_p \frac{\partial}{\partial x} (\rho u T) = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) - Q\dot{g} \tag{B7}$$

where we shall suppose that C_p is a constant throughout the paint. Q is a measure of the energy lost due to outgassing; this lost energy is

proportional to $\dot{g}$. In view of the continuity equation (B1), the energy equation may be written as

$$C_p \rho \left(\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + (C_p T - Q) \dot{g} \qquad (B8)$$

If we assume that energy is lost simply because of the removal of mass from the system, and that enthalpy changes intrinsic to the change in phase may be neglected, then

$$C_p T - Q = 0$$

and the source term in equation (B8) vanishes. This is the choice that we shall make in the sequel although it is not an essential restriction.

The model is completed by the specification of $\dot{g}$. The quantity $\dot{g}/\rho$ is the rate of mass loss per unit mass and can be reasonably assumed to be a function of T and $(m - m_f)$ where m_f is the final Lagrangian mass, a specified quantity. A possible choice is

$$\dot{g} = \rho D e^{-\Theta/T} H(m-m_f) (m-m_f)^\alpha, \ \alpha \geq 0 \qquad (B9)$$

where $(m - m_f)$ is the Lagrangian mass of potential gas still bound in the condensate.

B2. The Delta-Function Model

The equations described in Section B1 are unsatisfactory in several respects; certainly, the justification of equations (B2) and (B3) is weak. We shall bypass this flaw in the model by adding an additional assumption, one for which there is experimental evidence, namely that tumescence only occurs in a vanishingly thin zone. This is done by supposing that $\dot{g}$ is nonzero only at one temperature and, moreover, is very large at that temperature so that nonvanishing mass loss occurs. This is at variance with the experimental fact that mass loss occurs over a wide temperature range; such mass loss, unassociated with tumescence, could easily be accounted for, but we shall not do so at this time. This amounts to an assumption

that although mass loss may occur throughout the coat, only that responsible for tumescence is important, and it is localized.

With this assumption, the coating is divided into two regions separated by the front. Between the substrate and the front there is stationary material with uniform density. The temperature in this region is everywhere less than that at the front. Between the front and the free surface the material also has a uniform density, smaller than the initial value since all the material has been processed by the front. This density does not change with time. The temperature there is higher than that at the front, and the velocity is spatially uniform but is nonzero and varies with time. The only nontrivial equation on each side of the front is therefore the homogeneous energy equation,

$$\rho C_p \left(\frac{\partial T}{\partial t} + u\, \frac{\partial T}{\partial x} \right) = \left(\frac{\partial}{\partial x}\ k\, \frac{\partial T}{\partial x} \right) \qquad (B10)$$

where appropriate constant values for ρ, u, and k have to be assigned for the two regions. Connection or jump conditions across the front are deduced by an analysis of the front structure.

The location of the front is defined by

$$x = h(t) \qquad (B11)$$

and to examine its structure, we introduce the new variable ξ by means of

$$x = h + \delta\xi \qquad (B12)$$

δ is a small parameter that characterizes the thickness of the front. It is eventually set equal to zero.

The governing equations of Section B1 are now rewritten in terms of the independent variables ξ and t and, at the same time, expansions for the dependent variables are adopted of the form

$$T = T^* + \delta t$$

$$m \quad m \quad + \quad \ldots .$$

$$u \quad u \quad + \quad \ldots$$

$$\rho \quad \rho \quad + \quad \ldots$$

T^* is a constant since there is no significant change in temperature as the front is traversed, and m, u, ρ now stand for the leading terms in expansions in δ of the respective variables. The continuity equation (B1), equation (B5), and the energy equation (B8) now may be written to leading order in the form

$$\frac{\partial}{\partial \xi}(\rho u - \rho \dot{h}) = -\delta \dot{g} \tag{B13}$$

$$(u - \dot{h}) \frac{\partial m}{\partial \xi} = -\frac{m}{\rho} \delta \dot{g} \tag{B14}$$

$$\frac{\partial}{\partial \xi}\left(k \frac{\partial t}{\partial \xi}\right) = (C_p T^* - Q) \, \delta \dot{g} \tag{B15}$$

In equation (B14) the factor $(1 + f)$ has been replaced by m/ρ in order to make clear that the subsequent conclusions do not depend on any assumptions about the expansion process, other than that it is localized.

Comparing equations (B13) and (B14), we have

$$\frac{1}{m} \frac{\partial m}{\partial \xi} = \frac{1}{(\rho u - \rho \dot{h})} \frac{\partial}{\partial \xi} (\rho u - \rho \dot{h}) \tag{B16}$$

which may be integrated to yield

$$m = C(t) \, (\rho u - \rho \dot{h}) \tag{B17}$$

The solution within the front must match with the outer solutions on each side so that equation (B16) must be consistent with the conditions

$$\underline{\xi \to -\infty} \quad m \to m_o, \ \rho \to \rho_o, \ u \to 0$$
$$\underline{\xi \to +\infty} \quad m \to m_f, \ \rho \to \rho_f, \ u \to u_f(t) \tag{B18}$$

Here the subscript zero refers to the initial or virgin state, and the subscript f refers to the final state after tumescence has occurred. In this way we deduce the result

$$u_f(t) = \dot{h} \left[1 - \frac{\rho_o m_f}{\rho_f m_o} \right] \tag{B19}$$

which relates the instantaneous speed of the coating behind the front to the instantaneous speed of the front itself.

Finally, integration of equation (B15) across the front leads to the condition

$$\left[k \frac{dT}{d\xi} \right] = \frac{\rho_o}{m_o} (Q - C_p T^*) \dot{h} \; [m] \tag{B20}$$

which, together with the condition

$$[T] = 0; \quad T = T^* \tag{B21}$$

completes the specification of the connection conditions. Here the square bracket denotes conditions evaluated on the processed side of the front minus evaluation on the virgin side.

B3. **Nondimensional Formulation and Reduction to a Stefan Problem**

The problem of solving the energy equation (B10) on each side of the front together with the jump conditions (B19) – (B21), appropriate boundary conditions at the substrate boundary and the free (outer) surface, together with initial conditions, is a generalized Stefan problem. It is generalized in the sense that there are two boundaries whose locations have to be determined as part of the solution, namely the front and the outer surface. In this section, we shall formulate an equivalent nondimensional problem and then, by means of an elementary transformation, reduce it to one with but a single unknown surface.

Consider the details of the specific problem that we shall consider. Initially, the coating has a uniform temperature, less than T^*, and a thickness d. A heat flux is applied to the outer surface, in this way raising the temperature of the paint. After a time, t_1 has elapsed the

temperature at the outer surface reaches the value T*, signalling the
onset of tumescence. We shall call this initial period, occupying the
time interval $(0, t_1)$, the preheat phase.

Continuing application of the heat flux now causes the intumescent
front to move into the interior of the paint. This continues until the
front reaches the substrate at a time t_2. We shall call the interval
(t_1, t_2) the tumescent phase. At the end of it the paint has thickness D.

The final, or post-tumescent phase, is similar to the preheat phase
in the sense that it is characterized simply by an increase in temperature.
The coating is, of course, thicker, and its physical properties are differ-
ent.

Consider the tumescent phase. During this period, the outer front
moves a distance (D-d) at a speed $u_f(t)$, and the intumescent front moves
a distance d with a speed h. Thus,

$$D-d = \int_{t_1}^{t_2} u_f dt \quad \text{and} \quad d = -\int_{t_1}^{t_2} \dot{h}\, dt \tag{B22}$$

It follows from equation (B19) that

$$\frac{D}{d} = \frac{\rho_o m_f}{\rho_f m_o} \tag{B23}$$

whence equation (B19) may be written as

$$u_f = -\left(\frac{D}{d} - 1\right) \dot{h} \tag{B24}$$

The location of the free surface is then

$$x = L(t) = D - h(t)\left(\frac{D}{d} - 1\right) \tag{B25}$$

Since $m_o = \rho_o$ and $m_f = \rho_f D/d$, the jump condition (B20) becomes

$$\left[k \frac{\partial T}{\partial \xi}\right] = \dot{h}\left(\rho_f \frac{D}{d} - \rho_o\right)(Q - C_p T^*) \tag{B26}$$

In order to nondimensionalize the equations, we shall use d for the characteristic length, $\rho_f C_p d^2 / k_f$ for the characteristic time, and T^* for the characteristic temperature. At the same time, it is convenient to define certain nondimensional parameters by the formulas

$$\alpha = \frac{\rho_o k_f}{\rho_f k_o} \ , \ \ \sigma = \frac{D}{d} \ , \ \ p = \frac{k_o}{k_f} \ , \ \ q = \frac{\rho_o}{\rho_f} \ , \ \ \hat{Q} = \frac{Q}{C_p T^*} \qquad (B27)$$

With T, x, t, h, and L now standing for nondimensional variables, the problem may be written in the form

$$0 < x < h \qquad\qquad\qquad \alpha \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} \qquad\qquad (B28)$$

$$h < x < L \qquad\qquad \frac{\partial T}{\partial t} - (\sigma - 1) \ \dot{h} \frac{\partial T}{\partial x} = \frac{\partial^2 T}{\partial x^2} \qquad (B29)$$

During the preheat phase h=L=1, during the post-tumescent phase h=0, L=σ. Boundary conditions at the front are

$$T = 1; \ \frac{\partial T}{\partial x} (h^+, \ t) - p \frac{\partial T}{\partial x} (h^-, \ t) = (\sigma - q) \ \dot{h} \ (\hat{Q} - 1) \qquad (B30)$$

The conditions at the substrate and the free surface depend on the application; we shall suppose that the substrate is insulated and the energy flux at the outer surface is constant. Thus,

$$x = 0 \qquad\qquad\qquad\qquad \frac{\partial T}{\partial x} = 0 \qquad\qquad\qquad (B31)$$

$$x = L \qquad\qquad \frac{\partial T}{\partial x} = E \qquad or \qquad \frac{\partial T}{\partial x} = pE \qquad (B32)$$

There are two possibilities at x=L, depending on the nature of the material at the free surface. Until the surface temperature has been raised to the value 1, the material is virgin and has a conductivity k_o; after tumescence has started the conductivity is k_f.

We shall make the choice $\hat{Q}=1$ (cf. Section B1). Then the energy equation may be written in conservation form as

$$a \frac{\partial T}{\partial t} - b(\sigma - 1) \ \dot{h} \frac{\partial T}{\partial x} = \frac{1}{k} \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \qquad (B33)$$

where the parameters a, b, and k have the following values:

$$0 < x < h \qquad\qquad a = \alpha, \quad b = 0, \quad k = p$$

$$h < x < L \qquad\qquad a = 1, \quad b = 1, \quad k = 1 \qquad\qquad (B34)$$

Equation (B33) is valid everywhere, including the front, consistent with the jump conditions (B30).

Consider now the new variable defined by the formulas

$$0 < x < h \quad s = x \qquad\qquad\qquad h < x < L \qquad s = \frac{x}{\sigma} + \frac{\sigma - 1}{\sigma} h(t) \qquad (B35)$$

If s is used instead of x, equation (B33) becomes

$$\frac{ak}{s_x} \frac{\partial T}{\partial t} = \frac{\partial}{\partial s} \left(ks_x \frac{\partial T}{\partial s} \right) \qquad\qquad (B36)$$

which is to be solved on the fixed domain $0 < s < 1$. Boundary conditions at s=0,1 have the form

$$\underline{s = 0} \;\; \frac{\partial T}{\partial s} = 0 \;, \quad \underline{s = 1} \;\; \frac{\partial T}{\partial s} = E \qquad \underline{or} \quad \frac{\partial T}{\partial s} = \sigma p E \qquad (B37)$$

Equation (B36) is equivalent to the system

$$\underline{0 < s < h} \qquad\qquad \alpha \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial s^2} \;, \qquad \underline{h < s < 1} \qquad\qquad \sigma^2 \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial s^2} \quad (B38)$$

with jump conditions at the front (if h is an interior point)

$$[T] = 0, \quad \frac{\partial T}{\partial s} (h^+, t) = \sigma p \frac{\partial T}{\partial s} (h^-, t) \qquad\qquad (B39)$$

This defines a Stefan problem with a single unknown boundary.

B4. **Analysis**

(i) Preheat phase: heating of the virgin material.

During this phase it is necessary to solve equation (B28) subject to the boundary conditions (B31) and (B32a), and appropriate initial conditions. The latter will be taken to be

$$T = T_0 \quad (\text{a constant}) \quad \text{at } t = 0$$

The solution obtained using a Laplace transform in t is

$$T = T_0 + \frac{E}{\sqrt{a}} \frac{1}{2\pi i} \int_{Br} ds \; \frac{e^{st} \cosh \sqrt{as} \; x}{s^{3/2} \sinh \sqrt{as}} \tag{B40}$$

This is not a useful representation for finite time, but it does provide a description for very large times, namely

$$T \sim \frac{E}{a} t + \frac{1}{2} Ex^2 + T_0 - \frac{1}{6} E + o(1) \tag{B41}$$

This provides a characterization of the effectiveness of a coating which cannot intumesce.

A description for finite time is best obtained by numerical means. The procedure adopted was the method of lines described by Meyer (19). To this end, implicit differencing in time leads to the equation

$$\frac{d^2 T_n}{dx^2} - \frac{a}{\Delta t} T_n = - \frac{a}{\Delta t} T_{n-1} \tag{B42}$$

where T_n is the temperature evaluated at the time t_n. The problem is now imbedded in a one-parameter family which satisfies equation (B42) together with boundary conditions

$$T_n(o) = B, \quad T_n'(o) = 0 \tag{B43}$$

The parameter is B; for one choice of B, initially unknown, the associated temperature is the solution to our problem. In view of the linearity of the field equation, we may write

$$T' = PT + Q \tag{B44}$$

where the functions P, Q are independent of B. Substitution into (B42) and use of the boundary conditions (B43) leads to the initial value problems

$$P' + P^2 - \frac{\alpha}{\Delta t} = 0 , \quad Q' + PQ = - \frac{\alpha}{\Delta t} T_{n-1} \qquad (B45)$$

$$P(0) = Q(0) = 0$$

which are easily integrated using the trapezoidal rule.

At the free surface, the temperature of interest is given by

$$T_n(1) = [E - Q(1)] / P(1) \qquad (B46)$$

Consider equations (B32a) and (B44). This provides the initial condition for the integration of equation (B44) back towards the origin which completes the determination of T_n. Time is now advanced and the procedure repeated.

At $t = t_1$ the temperature at the free surface reaches 1. This yields the temperature distribution for the initial condition for the tumescent phase. Note that a good approximation of t_1 can be gotten from (B41) by letting $r=1$, $T=1$ and solving for t.

(ii). Tumescence.

During this phase, it is necessary to solve equations (B37) – (B39). The treatment of the virgin material proceeds as in phase (i) up to and including the calculation of P and Q. The solution of equation (B38b) between the front and the free surface proceeds in a similar fashion so that writing

$$T' = RT + S \qquad (B47)$$

leads to initial value problems for R and S in the form

$$R' + R^2 - \frac{\sigma^2}{\Delta t} = 0 , \quad S' + RS = - \frac{\sigma^2}{\Delta t} T_{n-1}$$

$$(B48)$$

$$R(1) = 0 \qquad S(1) = p\sigma E$$

These also are integrated using the trapezoidal rule.

The postion of the front can now be determined. The jump condition (B39b) implies that, at the front,

$$(R + S) - \sigma p \, (P + Q) = 0 \tag{B49}$$

It is a simple matter to determine where this function vanishes. Once the front location is known (linear interpolation between mesh points is necessary), equations (B44) and (B47) are integrated away from the front using the condition there that $T = 1$. In this way the new temperature is determined everywhere, and we may advance time and repeat the procedure.

In order to start this calculation, it is necessary to have an early time description, valid immediately after tumescence has started. The initial temperature on the cold side of the front comes from the phase (i) calculation. Initial conditions on the hot side of the front can only be determined after an analytical calculation of the initial speed of the front. To this end, we consider the solution for P and Q in the limit as $\Delta t \to 0$. We have

$$P \sim \sqrt{\frac{\alpha}{\Delta t}} + (\text{exponentially small terms}) \tag{B50}$$

$$Q \sim \sqrt{\frac{\alpha}{\Delta t}} \left[- T_{n-1} + \frac{\Delta t}{\alpha} T'_{n-1} - \frac{\Delta t}{\alpha} T''_{n-1} + \ldots \right] \tag{B51}$$

At a time Δt after tumescence has started, T_{n-1} is the final phase (i) solution which, for x close to 1, can be approximated by

$$T_{n-1} \sim 1 + E(x-1) + \frac{T''_{n-1}(1)}{2} (x-1)^2 + \ldots, \qquad T''_{n-1}(1) = \alpha \frac{\partial T}{\partial t} (1, t_1) \tag{B52}$$

If $(x-1)$ has the same order of magnitude as Δt, it follows that

$$(P + Q) \sim \sqrt{\frac{\alpha}{\Delta t}} \left[\sqrt{\frac{\Delta t}{\alpha}} E - E(x-1) - \frac{\Delta t}{\alpha} T''_{n-1}(1) \right] + O(\Delta t) \tag{B53}$$

Therefore, if h is given by

$$h \sim 1 - C\Delta t \tag{B54}$$

where C is the initial speed of the front, (P+Q) at the front is given by

$$(P + Q) \big|_h \sim E + EC\sqrt{\alpha\Delta t} - \sqrt{\frac{\Delta t}{\alpha}} \, T_{n-1}''(1) + \ldots \tag{B55}$$

Consistent with (B54),

$$(R + S) \big|_h \sim p\sigma E + O(\Delta t) \tag{B56}$$

and substituting (B55) and (B56) into (B49) shows that

$$C = \frac{T_{n-1}''(1)}{\alpha E} = \frac{1}{E}\frac{\partial T}{\partial t}(1, t_1). \tag{B57}$$

Thus, shortly after tumescence has started, the hot side solution is described by

$$T \sim 1 + \sigma p E \, [s - 1 + C(t-t_1)]$$

(iii) Fully Charred Phase.

This phase starts when the reaction front reaches the substrate. Clearly, we must solve (B38b) subject to $T_s(0,t)=0$, $T_s(1,t) = \sigma p E$ and the initial temperature being whatever the tumescent phase ended with. In the spirit of (B41), we may write

$$T \sim \frac{pE}{\sigma} (t-t_2) + \frac{\sigma p E}{2} s^2 + 1 + o(1) \tag{B58}$$

where t_2 is the time at which $h = o$.

We can see from (B58) that the temperature rises linearly with time at the plate, as it did in the preheat phase, but since

$$\frac{p}{\sigma} = \frac{k_o}{k_f}\frac{d}{D} = \frac{k_o}{k_f}\frac{\rho_f}{\rho_o}\frac{m_o}{m_f} = \frac{1}{\alpha}\frac{m_o}{m_f} > \frac{1}{\alpha} \tag{B59}$$

the rate can be higher depending upon the value of α.

This last result is counterintuitive if one's intuition is inspired by attic insulation practice. In point of fact, with a constant heat flux prescribed at the free surface of the paint, it is the thermal inertia of the layer at any instant which is important. What with the considerable

mass loss accompanying the swelling, the final char—being as porous as
it is—is not as good an insulator as the original thin coat of paint.
However, the char thermal conductivity is less than that of the original
material, which wants to retard the heat flux. Hence, whether or not the
char is an effective insulator depends upon two physical characteristics of
the char, the thermal conductivity and final expansion thickness.

B5. <u>Conclusion</u>

A nonreactive layer of paint would lead to a substrate temperature
which grew linearly with time. The moving reaction front results in a
much slower substrate temperature growth--almost a plateau. The final
porous char allows the substrate temperature to <u>resume</u> its linear growth
at a rate even faster than the original paint.

The reason for the plateau is quite clear from our frontal model.
The front is hotter than the substrate so that there is a heat flux from
one to the other. This flux persists until the non-dimensional substrate
temperature is virtually equal to 1, and as long as the front exists,
the substrate must wait to reach a temperature of 1.

The duration of the intumescense depends on the propagation speed
of the front which in turn is a function of the properties of both the
swollen and unswollen material. Moreover, while the plateau period will
increase with the endothermicity of the intumescence, there will be a
plateau even for a nonendothermic process.

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